Bioenergy Technologies and Strategies - A New Frontier

by Joyce C. Yang, PhD

INTRODUCTION

"O beautiful for spacious skies, for amber waves of grain; for purple mountain majesties, above the fruited plains…" – Katherine Lee Bates (1904)

The bounties of American ingenuity, climate and soil have combined synergistically not only to inspire the opening verse of a patriotic song but also to establish the United States as the world leader when it comes to agriculture[a] and forestry[b] productivity. Thus, it should not surprise us that researchers, engineers, industrialists, and policy makers have turned to our abundant biomass resources to reduce consumption of fossil energy, be that coal, natural gas, or petroleum. In fact, of all forms of renewable energy consumed in the United States, none rivals the amount of energy produced from biomass (Figure 1, combining wood and biofuels). A recent report estimates an additional renewable resource of one billion dry tons of agricultural residues, woody biomass and new energy crops that can be sustainably harvested every year (U.S. Department of Energy, 2011).

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[a] http://www.fas.usda.gov/wap/current/default.asp
[b] http://www.fao.org/forestry/statistics/80938@180723/en/

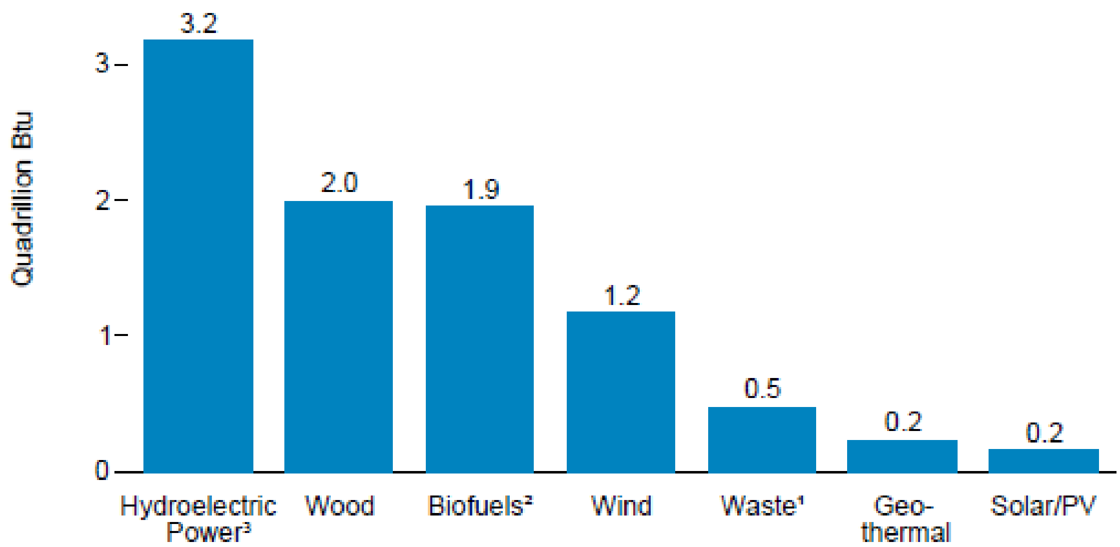

FIGURE 1. Renewable Energy Consumption in the United States by Source. Adapted from Energy Information Agency Annual Energy Review, 2011

BACKGROUND

The mission of the Bioenergy Technologies Office (BETO) within the U.S. Department of Energy (DOE) is to transform the available domestic biomass resource into fuels, chemicals and power. BETO achieves its mission through a diverse and comprehensive set of applied R&D programs, and first-of-a-kind technology demonstrations in a range of engineering scales called integrated biorefineries (IBRs). The overall BETO strategy is to sufficiently de-risk biofuel technologies by demonstrating feasibility, process robustness, process control, and scalability to attract private capital for further commercialization and market entry. BETO partners are encouraged to use feedstocks that do not compete with food or feed uses, and to develop a suite of versatile conversion technologies that can be deployed in as many regions of the Unites States as possible to maximize national benefit while providing an optimal regional solution.

Terrestrial biomass feedstocks are typically composed of three major types of polymers: cellulose (homogeneous polymer comprised of six-carbon sugars, or C_6s), hemicellulose (heterogeneous polymer but predominantly composed of five-carbon sugars, or C_5s), and lignin (heterogeneous polymer composed of a significant component of aromatic molecular units). Aquatic biomass, such as algae and cyanobacteria, can be a mixture of C_5s and C_6s polysaccharides, along with other classes of biopolymers such as proteins and lipids. Biofuels derived from terrestrial feedstocks are often referred to as “cellulosic” after its principle biomass component. This is in contrast to “conventional” biofuels, which are grain-based (e.g. corn ethanol) and do compete with the food and feed markets. BETO is currently focused on technologies that seek to use cellulosic or algal biomass feedstocks due to more favorable environmental benefits such as demonstrated by a life-cycle analysis of greenhouse gas emissions (GHG) and lower water consumption. In fact to qualify as a cellulosic biofuel for incentives a 60% GHG reduction must be achieved relative to gasoline. [1,2]

Biomass is transformed to biofuels in typically one of two processing routes- biochemical or thermochemical. For biochemical routes, biomass is typically first pretreated with chemicals, thermal or mechanical forces to open up the plant cell wall and structure. The pretreatment allows the partially depolymerized material to be exposed to microbial enzymes (cellulases and hemicellulases) that attack the chemical bonds to finally yield largely monosaccharides. These dilute sugar intermediates are usually fed to a microbe to yield fuels or more refined chemicals. For thermochemical routes, the biomass is typically mechanically preprocessed to specific sizes, inorganic contents, and moisture levels, and then subjected to moderate to high pressures and temperatures (with or without catalysts) to generate syngas or bio- oils intermediates. These process intermediates are cleaned or stabilized and then exposed to fuel synthesis catalysts to either reassemble the C_1 units into hydrocarbons or deoxygenate and hydrocrack larger biomass thermal derivatives to generate fuel blendstocks.

CURRENT STATUS

The Department of Energy announced the completion the several major R&D programs on cellulosic ethanol at the close of 2012. The validation of research and development achievements on both the biochemical and gasification routes to cellulosic ethanol confirmed the dramatic reduction in the modeled minimum ethanol selling price from more than $9/gallon when the Program began in 2002 to $2.15/gallon or less in 2012. The many technical performance improvements include better feedstock quality and logistics, pretreatment technologies, more productive cellulolytic enzymes, gas clean-up technologies, and the development of robust microbial and inorganic fuel synthesis catalysts, not to mention a wealth of enabling knowledge gains and breakthroughs as contributed by the awardees of the DOE Office of Science, National Science Foundation, the National Institute of Standards and Technology, as well as the Unites States Department of Agriculture.

Concurrent with the R&D achievements that correlated to driving down key biofuels cost factors, four first-of-a-kind integrated biorefineries focused on cellulosic ethanol were established in the United States. These facilities either began producing fuel or will begin to produce fuel next year (Table 1). One facility has begun to produce cellulosic "drop-in" hydrocarbon fuels. These IBRs represent far more than their technological components; each is also the result of successful process integration, scale-up, and constructions, as well as other critical success elements- feedstock contracts, project management, fuel off-take agreements, seasoned senior management, regulatory clearance and financing. Financing these biorefineries has been particularly challenging as the economics are as yet unproven.

TABLE 1. Commercial-Scale U.S. Integrated Biorefineries Constructed or Actively Being Constructed That Are Focused on Cellulosic Biofuels

	Ground Broke	Feedstock	Target Product	Process Type	Location	DOE Role
DuPont	2012Q4	Ag residue	Cellulosic ethanol	Biochemical	Nevada, IA	R&D
POET-DSM	2012Q1	Ag residue	Cellulosic ethanol	Biochemical	Emmetsburg, IA	R&D, IBR
Abengoa	2011Q4	Ag residue	Cellulosic ethanol	Biochemical	Hugoton, KS	IBR
KiOR	2011Q2	Southern pine	Cellulosic gasoline, diesel and jet	Thermo-chemical	Columbus, MS	None
INEOS-Bio	2011Q1	MSW, citrus waste, yard waste, woody biomass	Cellullosic ethanol	Hybrid	Vero Beach, FL	R&D, IBR

MOVING FORWARD

As early as 2010, BETO began to shift away from a singular focus on cellulosic ethanol to embrace a more holistic biofuels strategy to replace the entire barrel of oil by targeting the production of hydrocarbon, or "drop-in", fuels that are compatible with the current infrastructure. While ethanol can displace the gasoline used for light-duty passenger cars, it cannot be currently blended with other transportation fuels. One particularly interesting variation of the hydrocarbon fuel strategy is to produce an "intermediate" that is compatible with various insertion points within traditional petroleum refineries as depicted by the National Advanced Biofuels Consortium (Figure 2). The key advantage of this strategy is that several units of operations could potentially be avoided by leveraging existing assets of the petroleum refinery thus significantly lowering capital costs. There is also a fuel distribution advantage with the biomass derived blend stock strategy.

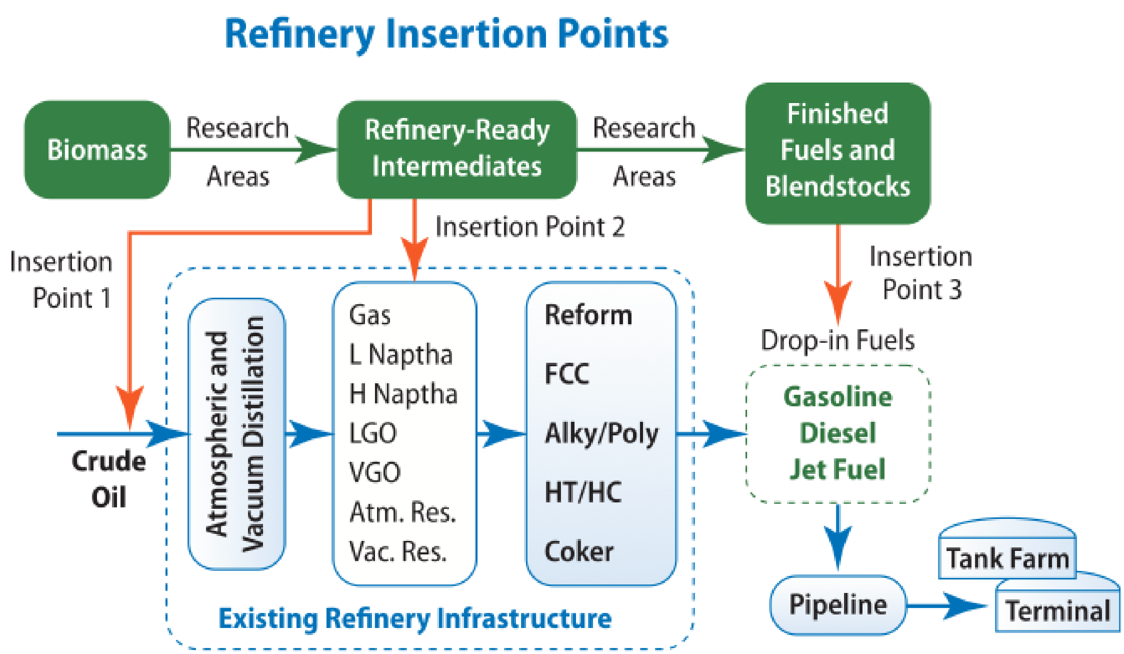

FIGURE 2. Proposed insertion points of biomass-derived fuel intermediates (taken from the National Advanced Biofuels Consortium website).

At least one major technical challenge exists with the new hydrocarbon biofuels strategy: stoichiometry.

Biomass is a relatively oxygen-rich carbon feedstock; hydrocarbons lack oxygen. When the target molecule was ethanol, biomass was an advantaged feedstock compared to petroleum based on basic stoichiometry. When the target molecule is a longer carbon chain with no oxygen, a biomass feedstock is disadvantaged. This basic chemical balancing act, illustrated in table form (Table 2) will be the key challenge moving forward requiring innovations across the biomass to biofuel supply chain.

TABLE 2. Stoichiometry of biomass and crude oil vs. biofuel options

	Biomass (1C:1O)	Crude Oil (>80C:1O)
Elemental Feedstock Composition (wt %)	C=44-51% H=5-7% O=41-50%	C=83-87% H=10-14% O=0.05-1.5%
Elemental Ethanol Composition (C_2H_6O)	C=52% H=13% O=35%	C=52% H=13% **O=35%**
"Model" Hydrocarbon Product (50% C_8H_{18} and 50% $C_{12}H_{23}$)	C=85% H=15% **O=0%**	C=85% H=15% O=0%

The removal of oxygen within the biomass fuel intermediate will be essential for compatibility with existing crude oil processing streams; however, it certainly means significant loss of yield either in the form of water (requires a hydrogen source) or carbon monoxide or dioxide (even more loss of yield from the original biomass). Hydrogen can be derived from methane reforming, however, the impact on the GHG reduction for this option should be considered. On the other hand, losses of carbon as CO2 is also unpalatable, and will negatively impact the GHG profile.

At least one partial solution is to diversify the product slate. If hydrocarbon fuels cannot contain oxygen molecules, then it's possible that a marketable co-product that is "oxygen-rich" (defined for the purposes of this report as having a C:O ratio less than 1) can be made alongside the fuel. It's also likely that such a co-product could enhance the economics of the overall conversion process. The Department of Energy identified several such value-added chemicals in the widely acclaimed "Top Value Added Chemicals from Biomass Report: Volume 1" from 2004, and the "Top Value Added Chemicals from Biomass Report: Volume 2" from 2007. Opportunities include but are not limited to sorbitol, xylitol, aspartic acid, and diacids.

The imbalance in C:O ratio in feedstock and product also requires ever more efficient utilization of the biomass resource itself. Losses that can occur under open storage systems (e.g. bale yards or wood laydown yards) to support year-round cellulosic biorefinery operations and year-by-year catastrophic natural disasters (droughts, flooding) will be unacceptable. Commoditizing the biomass feedstocks can be an effective mitigation strategy. A version of this advanced feedstock concept has been proposed by the Idaho National Laboratory (Figure 3).[3] A key aspect of this concept is that different feedstocks can be blended to pre-defined physiochemical specifications while being densified to facilitate logistics. While this commodity biomass feedstock will not be available without incurring additional costs due to the additional processing, it is the solution that bears the most resemblance to existing agricultural grain commodity system, raising the interesting possibility of leveraging the grain distribution network as another infrastructure cost reduction opportunity.

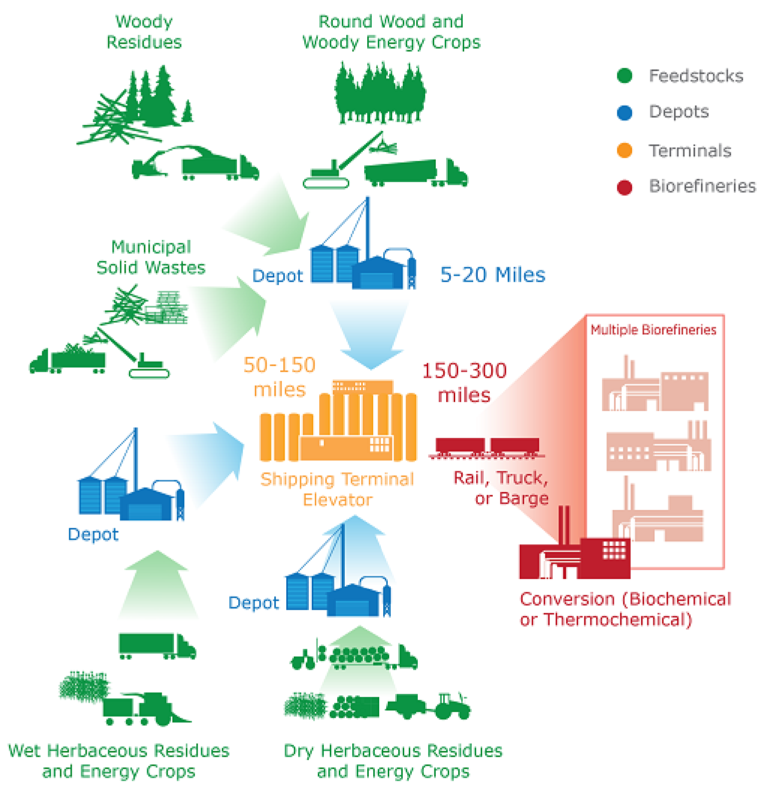

FIGURE 3. Supply logistics network of densified and commoditized preformatted biomass feedstocks (Source: Idaho National Laboratory)

Arguably the most intriguing of possible solutions is to create an advanced biomass feedstock or feedstock component that changes the overall C:O ratio *in vivo* to favor hydrocarbon fuel formation. A study published in 2007 suggested that natural plant and microbial oils, such as algal lipids, can be readily converted into hydrocarbon fuels or blendstocks using existing petroleum refinery units.[4] The current work on algae suggests that algal productivities could soon exceed palm oil (best terrestrial oilseed crop) productivities.[5] However, the cultivation and processing costs of the baseline notional algal systems results in a fuel product cost that exceeds $18 per gallon. The relative advantages of using modified biological feedstocks as a means to achieve refinery-ready intermediates versus other approaches will need to be carefully evaluated both in terms of theoretical yields and practical considerations.

CONCLUSION

Over the past two decades, the United States has consistently pursued a RD&D and policy strategy to reduce the dependence on fossil fuels. Through policies such as the Energy Independence and Security Act of 2007 (Public Law 110-140), the Energy Policy Act of 2005 (Public Law 109-58) and the Biomass R&D Act of 2000 (Public Law 106-224, Title III), the federal government has supported innovators across the supply chain, culminating in the first U.S. commercial production of cellulosic ethanol in 2013. There is not only an abundance of renewable biomass, but also existing infrastructures we can better utilize in the country. The new frontier of biofuels RD&D will no doubt be full of significant challenges. However, the scientific and engineering innovators working in this space will overcome these challenges as they will be building upon the solid foundation of knowledge and leveraging the advancements already made in first and second generation biofuels.

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