Biomass as a Source of Carbon: The Conversion of Renewable Feedstocks into Chemicals and Materials

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The exceptional current interest in biorefinery development is intimately linked to the country's access to a large amount of renewable carbon in the form of biomass. Recent work has identified a sustainable biomass supply in the United States of 1.3×10^9 tons/year without upsetting normal supplies of food, feed and fiber, and without requiring extensive changes in infrastructure or agricultural practices (Perlack *et al*., 2005). The corn industry produces 8–10×10^9 bushels/year, each containing about 33 pounds of carbohydrate as starch, and equivalent to almost 500×10^6 barrels of crude oil (Varadarajan and Miller, 1999; NCGA, 2008), and the current surge of production of corn-based ethanol will drive production even higher. The pulp and paper industry converts over 240×10^6 tons/year of wood for the production of paper products (Anon, 2002). Cellulose, the most abundant organic chemical in the biosphere, is produced at an annual level of about 10^{10}–10^{11} tons (Hutchens *et al*., 2006). Second-generation facilities for ethanol production will rely on lignocellulose, and the renewable fuels standard has legislated cellulose as the source of 16 billion gallons of fuel ethanol by 2022 (RFA, 2008). The other primary component of lignocellulosic feedstocks, lignin, comprises up to 25% by weight of the biomass feedstock, and is a promising source of aromatic chemicals (Bozell *et al*., 2007). When measured in energy terms, the amount of carbon synthesized by plants is equivalent to about ten times the world consumption (Indergaard *et al*., 1989). Importantly, the cost of biomass raw material has been shown to be comparable to that of nonrenewable carbon sources on the basis of contained energy (Lynd *et al*., 1999, 2008).

Biorefinery Operation

The biorefinery concept has developed to unify the processes and technology necessary to convert this vast resource into chemicals and fuels. The biorefinery is exactly analogous to a petrochemical refinery, and contains three primary process operations (Fig. 1). First, the biorefinery requires a raw-material supply. Nature provides diverse potential feedstocks, ranging from well-recognized agricultural materials (wood, corn, soybeans) to more exotic materials such as guayule or regional processing streams. The supply component of the biorefinery is possibly the most complex when viewed in the context of petrochemical processing, as nonrenewable carbon supplies can frequently be described by the single terms “crude oil” or “natural gas.” Nonetheless, this perceived complexity largely disappears when it is realized that almost all renewable raw materials are sources of a much smaller group of more structurally defined biopolymers.

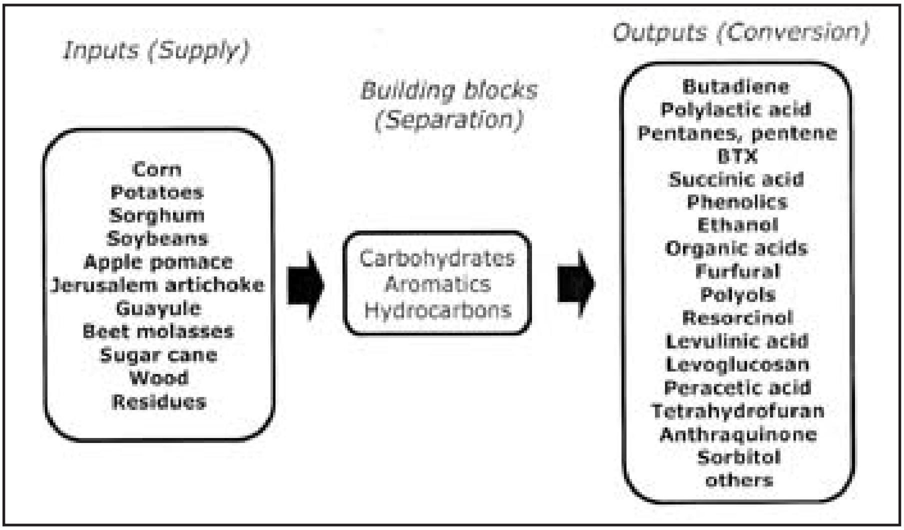

Figure 1. The three stages of biorefinery operation.

These biopolymers are isolated in the separation stage of biorefining, which generally provides three process streams: carbohydrates, in the form of starch, cellulose, hemicellulose and monomeric sugars, aromatics in the form of lignin, and hydrocarbons in the form of plant triglycerides. Separation processes in the biorefinery are closely related to pretreatment technologies normally associated with ethanol production (Sun and Cheng, 2002; Mosier *et al.*, 2005). As the concept of the modern, integrated biorefinery has evolved, pretreatment technology has also evolved from activation of a biomass feedstock for a monolithic biofuel operation into fractionation, where the various primary components of a given raw material might now be used in several different chemical or biochemical transformation processes.

The final operation in the biorefinery is conversion. In this stage, the intermediate building blocks from separation are subjected to a variety of conversion technologies, giving a family of biobased chemicals and fuels. Production of high-value products as part of the total output is important economically, as it allows the biorefinery to “afford” more costly—but perhaps more selective—upstream pretreatment/fractionation technologies.[1] However, it is also in conversion operations that the greatest difference between the petrochemical refinery and the biorefinery is found. For the most part, it is straightforward to collect either renewable or nonrenewable carbon (supply) and subsequently transform it into an initial set of primary building blocks (separation): ethylene, BTX (benzene, toluene and xylenes), *etc.*, from nonrenewables, or glucose, xylose, *etc.*, from renewables. However, the petrochemical industry has developed an impressive array of selective, high-yield structural transformations for the transit of crude oil to an initial set of simpler building blocks and eventually to the thousands of chemical products used by consumers. In comparison, a chemical industry hoping to use biomass as a raw material currently suffers from a much narrower range of discrete building blocks and fewer methods to convert those building blocks to other materials. *This technology gap is not the result of any inherently greater level of difficulty in processing of biomass.* Instead, it is the result of chemical-production research and technology to date being focused almost exclusively on highly reduced, oil-based hydrocarbons, rather than highly oxygenated carbohydrate-based materials. The increase in research interest in renewables in recent years is an effort to narrow this technology gap and develop methodology for renewable carbon as efficient as that available for nonrenewable carbon.

The Impact of Chemical Production Within the Biorefinery

Sustainable exploitation of the nation's domestic resources requires that the biorefinery address two strategic goals. First, the biorefinery's substitution of imported petroleum with domestic raw materials is primarily an *energy* goal. But realization of the energy goal requires a financial incentive to build facilities able to use renewables as feedstocks, to justify industrial use of new raw materials and to incorporate technology for their conversion. These incentives are the characteristics of an *economic* goal. The energy goal is addressed by biorefineries producing fuel, primarily fermentation ethanol. However, since fuel is a high-volume, low-value product, new, stand-alone fuel facilities are often burdened by a low return on investment, making their construction less desirable. For example, recent decreases in the profit margin for production of corn ethanol as a result of higher raw material costs in the United States has led to delay or cancellation of a number of ethanol-production projects. A biorefinery based on chemical products alone can realize a much higher return on investment, but lacks the potential for a large energy-displacement impact. This results in attempts to identify "blockbuster" products, the energy impact of which might be significant. However, few of these opportunities exist and chemical production accounts for only about 7–8% of our oil imports (Donaldson and Culberson, 1984). Various analyses (Dorsch and Miller, 2004; J. Bozell and A. Aden, unpublished results) reveal that producing both chemicals and fuels in an integrated biorefinery meets the energy and economic goals simultaneously. In an integrated operation, high-value products become an economic driver providing higher margins to support low-value fuel, leading to a profitable biorefinery operation that also exhibits an energy impact.

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[1] The use of terms such as "high volume" or "high value" is extremely subjective, as a "high-value" product to a fine chemical producer might be well over several dollars per pound, but considerably under a dollar for a commodity producer.

Pre-identification of Biobased Products vs. Broad Technology Development

Despite the projected impact of chemical production on the economic viability of the integrated biorefinery, current research on chemicals lags that on fuels. For example, programmatic funding for biobased-product development by the US Department of Energy (DOE) ended in 2006 (DOE, 2007). The single biggest barrier to chemical production within an integrated biorefinery is a lack of broad-based processes tailored for renewable process streams that demonstrate scope comparable to that available for petrochemicals. A significant contributing factor to this situation is that chemicals are a much more complicated segment than fuels. The great complexity inherent in chemical products accurately reflects the nature of the chemical industry itself, which is anticipated to be the primary customer for any technology development. Many approaches to biorefinery chemical production begin with a search among the huge number of potential opportunities and an attempt to pre-identify the best single, specific structures for research and development. Because of the broad diversity of materials currently supplied by today's chemical industry, and the basic structural differences between renewable and nonrenewable building blocks, this identification process frequently becomes mired in a confusing array of possibilities, fragmenting chemical development in the biorefinery. An alternative approach to this question results upon recognition of the marked difference between the production of chemicals and the production of fuels. The fuel component of the biorefinery is *convergent*, whereas the chemicals component is *divergent* (Fig. 2).

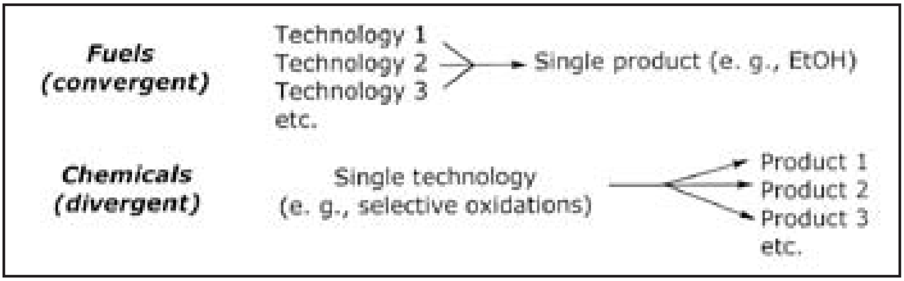

Figure 2. Fundamental differences between biorefinery fuel and chemical production.

The high-volume fuel outputs of the biorefinery are primarily single-product operations, such as fermentation ethanol or syngas from biomass gasification. As well defined single products, such materials can be assigned highly specific cost targets, and can have a wide range of technologies applied to their production. Whether a given technology is adopted for production of these materials depends almost exclusively on how well it meets the cost targets. If the targets are missed, the technology is discarded in favor of other approaches with a better chance of achieving cost goals, making single-product studies convergent.

In contrast, biobased products are much more diverse, as would be expected based on the experience of today's petrochemical industry and the tens of thousands of products it offers to the market. The chances of picking a winner are small, making a product-by-product approach less effective. Moreover, technology development for products is different from that for single materials such as ethanol or syngas. It tends to be divergent, in that technology found unsuitable for one structure may be useful for another because the cost-structure and economic drivers for the two-product candidates may be entirely different. Accordingly, success in biobased-product development will result more readily from identification of broad-based technology best suited for biomass, and applicable to producing a range of potential structures from biorefinery process streams. An investigation based on broad technologies will have a better chance of identifying those structures most easily available from biomass, simplifying evaluation of their properties and potential industrial/commercial viability. This approach would model the early days of the petrochemical industry as it evolved from thermal cracking (with kerosene as a primary product) to steam cracking (with olefins as key products).

Thus, while it may prove difficult (or even impossible) to unambiguously define a specific chemical structure that is the ideal target in the early stages of an R&D effort, broad technology development can be coupled with a straightforward definition of broader characteristics that a successful product candidate exhibits. For example, a biobased product should:

- Address large market segments of the chemical industry
- Exhibit or duplicate properties already identified by the chemical industry as marketable and valuable
- Provide attractive price and production volume opportunities
- Be easily made in high yield and a minimum number of steps from the biomass raw material

BIOBASED PLATFORMS

A small but growing number (in comparison to those available from the petrochemical industry) of biobased products fit into these categories. Broad technology development has identified products such as sugar alcohols (catalytic reduction) and acids (catalytic oxidation), furfural, hydroxymethylfurfural (Zhao *et al.*, 2007), and levulinic acid (dehydration) (Bozell *et al.*, 2000; Fitzpatrick, 2006), acetone, butanol, ethanol (Ezeji *et al.*, 2004) and lactic acid (fermentation) (Danner and Braun, 1999), or fatty acid hydrocarbons and glycerol (transesterification). Further, if a candidate product is made in a single step from biomass, it has the potential for use as a primary platform chemical within the biorefinery, serving as a starting material for the production of a much larger family of derivatives. Currently, somewhat less is known about the types of markets biobased products will address, or the types of properties the products may exhibit, but by examining their structure, a categorization of potential uses can be made. Recent DOE "Top 10" reports on products from biorefinery carbohydrates or lignin (Werpy and Petersen, 2004; Bozell *et al.*, 2007) have examined the combination of broad technology needs with an initial list of potential biorefinery product structures. A conclusion from these reports is that success in technology development will provide methodology applicable to a much wider number of compounds than the initial "Top 10."

Characteristics closely linked to choice of biobased products are appropriate price and volume targets for new materials. Too high a price on a product relegates it to extremely low-volume niche materials (*e.g.*, pharmaceuticals), and lessens its potential to provide an economic incentive for biorefinery development. Price and volume predictions seem to suggest a need to identify specific structures for evaluation. But can realistic bounds be set on a product from a huge number of potential candidates? A high-level answer to this question can be obtained by examining the product choices historically made in the petrochemical industry and business models adopted. Sources such as the Chemical Economics Handbook (SRI, 2008) provide product-manufacturing information from dozens, if not hundreds, of chemical companies worldwide. Information on compounds and materials that are viewed as most important to the success of the chemical industry is available. Figure 3 provides a plot of about 125 different chemicals and polymers produced by the petrochemical industry. Several chemical and polymer products are labelled as reference points.

As expected, Fig. 3 shows a general correlation between reported prices and volumes. The highest-volume materials tend to be cheaper, with the prices exhibiting a floor of about \$0.20/lb, even at the highest volumes (2003–2005 data). However, 85% of these materials cluster between 30 million tonnes/year and less than \$2.00/lb. Of these materials, 65% cluster below 10 million tonnes and less than \$1.00/lb. Additional subsets of these materials can be pulled from the data to give more specific categories. Although not shown in Fig. 3 or 4, a cluster of materials used primarily as polymer precursors

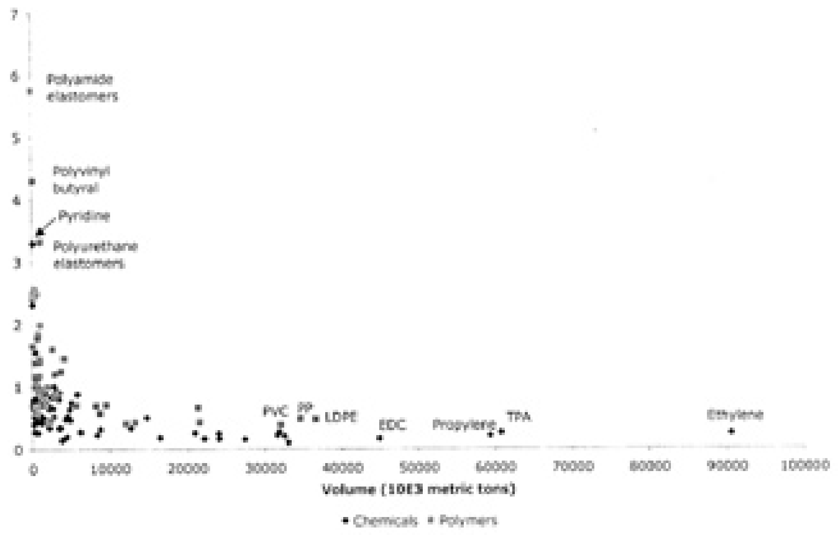

Figure 3. Correlation of chemical and polymer volumes with price (\$/lb) (2003–2005 data).

appears between \$0.35–0.75/lb, and less than 5 million tonnes/year. Despite this being a simplistic approach, industrial data provide some potential initial cost and volume targets for biorefinery chemicals. Figure 4 expands the area of Fig. 3 for chemicals with production volumes less than 30 million tonnes/year and costs less than \$2.50/lb. Most of the chemical industry's important products, as defined in the *Chemical Engineering Handbook*, are produced to meet costs of less than \$1.00/lb and production volumes less than 10 million tones, as shown within the circle in Fig. 4. Expanded, second-generation targets may be based on the needs of the biorefinery operator, such as materials inside the oval in Fig. 4.

Combining the technology needs identified in reports such as the DOE "Top 10" evaluations with first-approximation evaluations of price and volume for bioproduct development provides general characteristics of potentially successful biobased materials. As technology appropriate for bioproduct development improves, and the number of structures easily obtainable from biomass increases, the results of R&D activities can be subjected to high-level screens that suggest that if 1) a structure's production cost plus profit is less than \$1.00, 2) production can be scaled to around 5×10^6 tonnes/year, and 3) the product exhibits properties meeting or exceeding those already in the marketplace, an industrially viable compound may result. Improved technology will also result in improved economic evaluation and process analysis so that biorefinery operators will have the best combination of technology and economic information to make informed decisions regarding product choice.

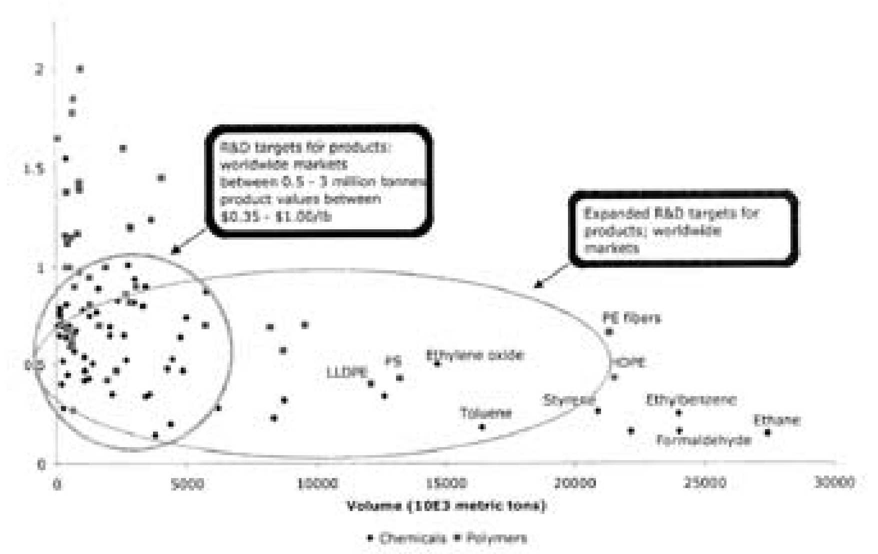

Figure 4. Potential cost (\$/lb) and volume targets for biobased products.

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His primary research interest is in using the tools of organic chemistry to develop technologies for converting renewable materials (biomass, carbohydrates, lignin, lignocellulosics) into chemical products and polymers.

Dr. Bozell has served as editor of two ACS symposium series assessing chemicals from biomass opportunities, has organized two ACS symposia on the use of renewables for chemical production, and is an editor of the Wiley journal *CLEAN – Soil, Air, Water*. He has numerous peer-reviewed publications, meeting and symposium presentations, and has delivered a number of invited lectures on the topic of chemicals from renewables. In 1999, he was a co-recipient of the Environmental Protection Agency's Presidential Green Chemistry Award.