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Cellulosic Biofuels: Importance, Recalcitrance, and Pretreatment

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2.1 Our Place in History

The two most profound societal transformations in history have been spawned by radical shifts in humankind's use of natural resources. The agricultural revolution, which spanned about two millennia beginning around 4000 BC, saw hunter-gatherer societies subsisting on wild plants and animals being largely displaced by those cultivating the land to produce crops and domesticated livestock. The industrial revolution followed, beginning around 1700 and lasting roughly two hundred years, during which time preindustrial agricultural societies gave way to those harnessing precious metals and fossil energy to develop sophisticated economies centered around machinery and factories. Now, with ever-increasing indications that resource use is exceeding the world's sustainable capacity, it is clear that a third revolution – the sustainability revolution – must begin soon and must be completed in decades, not centuries [1]. A few centuries hence, we think it is quite likely that people will look at those of us alive today, observe that "It was pretty obvious at the start of the third millennium that humanity needed to rapidly shift from resource capital to resource income," and evaluate us largely on our success at meeting this defining challenge of our time.

2.2 The Need for Energy from Biomass

As the only foreseeable sustainable source of food, organic materials, and fuels that are liquid at atmospheric pressure, plant biomass is a central and essential component of a sustainable world. Whereas biomass can be converted to high-performance liquid fuels, other large-scale sustainable energy sources are most readily converted to electricity and heat. Due to energy density considerations, it is reasonable to expect that organic fuels will meet a significant fraction of transportation energy demand for the indefinite

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future. Biofuels are by far the most promising sustainable source of organic fuels and are likely to be a non-discretionary part of a sustainable transportation sector – especially for aviation and heavy-duty vehicles. It is very unlikely that anyone alive today will ride in a battery-powered jet.

In their recent analysis 'Transport Energy and CO_2', the International Energy Agency states "A revolution in technology will be needed to move toward a truly low CO_2 future. This will be built on some combination of electricity, hydrogen, and biofuels." Their BLUE Map scenario – which achieves CO_2 emissions that are 30% below 2005 levels through improvements in vehicle efficiency and introduction of advanced technologies and fuels – has biofuels responsible for about a third of total transport energy in 2050 through meeting 40% of light-duty vehicle (LDV) demand and 30% of trucking, aviation, and shipping demand. The remaining LDV energy will be met by electricity and hydrogen; petroleum fuels comprise the balance for trucking, aviation, and shipping [2]. It is notable that biomass is the largest primary energy source supporting humankind in the BLUE map scenario.

2.3 The Importance of Cellulosic Biomass

The choice of feedstock represents the most important factor impacting key bioenergy performance metrics including scale of sustainable production, productivity (i.e., yield/area/year), land availability, fossil fuel displacement, feedstock cost, conversion cost, and environmental impact. Regarding productivity, perennial cellulosic crops generally outperform annual row crops, which makes sense given that plants grow faster when their composition is optimized for photosynthesis rather than for producing components that are easy to digest or process (e.g., starch, sugar, oils). Cellulosic crops can also be grown on marginal land unsuitable for annual row crop production, reducing potential competition with food production. Biofuels production from cellulosic feedstocks offers greater potential for displacing fossil fuels, as cellulosics contain a significant fraction of energy-rich lignin that can be used to fuel the conversion process. In contrast, processes involving annual row crops typically require external fossil-energy inputs. Lignocellulosic feedstocks also appear to have a cost advantage relative to row crops and sugarcane. Corn, for example, is currently priced above \$5/bushel, equivalent to \$12/GJ, and soy oil at above \$0.50/lb, or \$30/GJ. Both commodities are likely to remain at these levels or higher for the foreseeable future. By comparison, cellulosic energy crops are likely to be valued at \$60–\$100/dry ton or \$4–\$7/GJ. Finally, cellulosic biofuels offer potentially greater environmental benefits relative to biofuels made from annual crops, including lower net greenhouse gas emissions, improved water use efficiency and water quality, reduced soil erosion, enhanced soil fertility, and more positive biodiversity attributes [3]. In fact, many view the use of perennial cellulosic species as essential to achieving sustainable agriculture for reasons beyond bioenergy production. For example, in their detailed discussion, Kahn *et al.* [3] state "Perennial crops would increase soil organic matter, reduce pollution, and stabilize soils against erosion. They would help fields, forests, and rangelands retain water, thereby reducing flooding and helping aquifers recharge. Perennials would also sequester large quantities of CO_2, helping to slow climate change."

2.4 Potential Barriers

There are two primary barriers to realizing the potential of cellulosic biofuels on a large scale: (1) the recalcitrance of cellulosic biomass and (2) land-use concerns, especially those regarding competition with food production. While a detailed treatment of the latter is outside the scope of this book, we and others envision scenarios (e.g., growing crops on abandoned land; growing cool-season grasses on the same land as row crops between fall harvest and spring planting; and improving the productivity of pastureland) that gracefully reconcile large-scale bioenergy production with other priorities. The Global Sustainable Bioenergy Project (http://bioenfapesp.org/gsb/), launched in 2009, seeks to develop and evaluate such scenarios.

The recalcitrance barrier is a matter of biological function. For seeds, upon which current biofuel production in temperate climates is based, the function is to provide energy for the next generation of plants to grow and, in this capacity, to resist decay for a brief period (usually during the winter). By contrast, the biological function of lignocellulose is to hold the plant up, often including elevating the "solar collector" (leaves) of one plant above that of a competing plant. In this capacity, decay must be resisted during the summer months and quite commonly for decades. Plant cell walls therefore contain three primary polymer types – cellulose, hemicellulose, and lignin – arranged in a complex, composite matrix involving multiple layers that provide structural support and recalcitrance to attack by both microorganisms and the elements. Given these divergent functions, it is quite understandable that the carbohydrates present in cellulosic biomass are much more difficult to access than the carbohydrates present in seeds. "Recalcitrance" refers to the difficulty of accessing the carbohydrate present in lignocellulose. Overcoming this recalcitrance is the central challenge to large-scale commercial production of cellulosic biofuels.

2.5 Biological and Thermochemical Approaches to the Recalcitrance Barrier

Two broad categories of conversion technologies exist for producing cellulosic biofuels: thermochemical and biological. Thermochemical conversion involves exposing biomass feedstock to high temperatures (e.g., 300–1200 °C) under oxygen-limited conditions that serve to break the biomass polymers into light-molecule fragments. Depending on the reaction conditions, the molecular fragments can repolymerize into oily compounds, form a carbon-rich solid residue known as char, and/or remain as a gas, rich in CO and H_2. Fuels suitable for transportation (e.g., methanol, ethanol, Fischer-Tropsch diesel and gasoline, and dimethyl ether) can be made from the gas and/or liquid bio-oil by downstream processing [4]. Meanwhile, biological conversion involves the production of cellulolytic enzymes that hydrolyze the cellulose and hemicellulose fractions of biomass and fermentation of the resulting sugars to fuel products such as ethanol and butanol. These steps can be conducted separately or in varying degrees of integration, with single-step conversion (referred to as consolidated bioprocessing or CBP) representing a potential breakthrough in low-cost processing [5].

Biological conversion processes typically offer much higher product selectivity than thermochemical processes. In producing ethanol, for example, biological conversion yields ethanol and CO_2 in equal proportions on a molar basis (and approximately so on a mass basis) – a molar ethanol selectivity of 50% – while thermochemical conversion results in many additional products such as methanol, propanol, butanol, and a mixture of alkanes with ethanol selectivity generally less than 20%. Because the heat of reaction to form ethanol is small and CO_2 has no calorific value, from a fuel perspective about 98% of the energy of the sugars ends up in the ethanol, thus concentrating energy. Yields are typically higher for biological processes as well. The additional products resulting from thermochemical processing also make product recovery more challenging than for biological processes. Meanwhile, thermochemical processes are more flexible with regard to feedstock; in principle, any carbonaceous material (including e.g., manures, waste oils, food waste, and animal refuse) can be gasified and converted to fuels. They also have the advantage of being robust, well-tested processes, and commercially available today. A detailed comparative study of mature biomass conversion technology concluded that biological processing will likely prove to be the lower-cost option for processing carbohydrate, with viable process economics able to be realized at smaller scales than for thermochemical processing [6].

Biochemical and thermochemical processing however need not – and, we think, should not – be viewed as mutually exclusive. Lignin-rich residues from biological processing of carbohydrate, for example, can be converted to fuels and/or power using thermochemical processing. This configuration has the advantage that most, if not all, steam and power inputs for biological conversion can be met largely by capturing waste heat from the thermochemical process. As suggested by this example, integrated configurations involving both biological and thermochemical conversion are in general more efficient than processes that only use biological or thermochemical processing. Analysis of foreseeable mature biomass conversion technologies indicates that the most efficient and profitable configurations combine biological and thermochemical processing. Such integrated processes have the potential to realize efficiencies on a par with petroleum-based fuels and achieve production costs competitive with petroleum fuels at about $30/barrel [6].

Realizing the considerable potential of cellulosic biofuels requires that the recalcitrance of cellulosic biomass be overcome in a cost-effective manner. In the case of promising biological conversion routes, this involves the two key components of pretreatment and enzymatic hydrolysis, the central focus of this book.

2.6 Pretreatment

Like any story, the story of pretreatment of cellulosic biomass can be told beginning at many starting points. One such point is a young scientist named Elwin Reese employed at the US Army Research Lab in Natick, Massachusetts. Alarmed by the short lifetime of canvas tents in tropical climates during World War II, Dr Reese was assigned to look at microbial degradation of cellulose. Together with Dr Mary Mandels and many colleagues, Dr Reese conducted pioneering work in the field for nearly three decades; this research notably involved an aerobic fungus originally named *Trichoderma viride*, but later renamed *T. reesei* in his honor. As Drs Reese and Mandels neared retirement, much had been learned and results on hydrolyzing newsprint were promising, but the problem of how to obtain high hydrolysis yields on lignocellulosic substrates was still unresolved.

In the late 1970s, Dartmouth Professor Hans Grethlein wrote a proposal to the National Science Foundation (NSF) to study dilute acid hydrolysis as a means of making biomass accessible to enzymatic hydrolysis. The idea was that combinations of temperature, residence time, and acid concentration could be found that were sufficiently severe to remove hemicellulose and thus make cellulose accessible to enzymatic attack, but sufficiently mild to not extensively degrade solubilized hemicellulose sugars (still a key tradeoff today). Interestingly, Elwin Reese was one of the reviewers in this proposal and expressed doubt that the process could be effective since cellulose crystallinity would not be decreased. The mechanistic basis for pretreatment effectiveness (and ineffectiveness) is still a subject of active research.

Beginning in the 1980s, studies at the Solar Energy Research Institute (now the National Renewable Energy Laboratory or NREL) established a foundation for the economic evaluation of biologically based processing of cellulosic biomass. Throughout many changes in configuration and advances in performance, and analyses by many groups all over the world, pretreatment has remained among the most costly process steps [6,7]. The cost of the operation, however, extends beyond capital and operating expenses for pretreatment *per se*, due to the multiple and often pervasive impacts on downstream processing.

These impacts arise from the reactivity of pretreated solids, inhibitory compounds present in pretreatment hydrolyzates, and – depending on the process – additional compounds associated with pretreatment that require either recovery (e.g., ammonia) or can lead to operational difficulties (e.g., gypsum). We note also that the fractional cost of pretreatment generally increases as the overall process develops, that is, as the biologically mediated steps improve and as conditions become more commercially viable (e.g., increasing solids concentration).

Notwithstanding the decades-long trajectory of research on pretreatment and related topics, the field has made great strides. These have been enabled by convergent factors, including radical advances in biotechnology and analytical chemistry and, over the last five years, much higher funding from both governments and the private sector in many countries (notably including the United States). Over the next decade, it will likely become clear whether or not humanity will look to biofuels to play a key role in the historic transition to a world supported by sustainable resources addressed at the beginning of this chapter. It is therefore a particularly opportune and indeed important time to collect leading pretreatment research, and the perspectives of leading pretreatment researchers, into a volume such as this.

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