

Agricultural Chemistry and Bioenergy

Renewable energy for transportation is capturing, finally, its share of the headlines, and all indications are that this will continue. There are several drivers: the cost and uncertain future supplies of fossil fuel, particularly petroleum-based fuels; the rising CO₂ levels in the atmosphere, arguing for new fuels which trend toward carbon-neutrality; the rapid development of commercial scale bioethanol refineries, with sugar cane (Brazil) and corn (U.S.) as primary feedstocks; and the growing use of vegetable-based oils as biodiesel substitutes for petroleum diesel. In some respects, these examples represent the 'low-lying fruit' harvested to meet the rising demand of the early 2000s for bio-based transportation fuel.

While corn starch, cane-derived sugar, and seed oils from agricultural sources can contribute to current and immediate future demands, they can not meet the expectations that biomass-derived fuels will affect, in a major way, the global "addiction to oil." Thus the focus on cellulosic biofuels - making use of the complex carbohydrates which form the very structure of the plant kingdom.

But conversion of cellulose and hemicellulosic carbohydrates to ethanol is not technically simple, the uncertain and slow step being conversion of complex carbohydrates to readily fermentable monomer sugars. This conversion will require new pretreatment technologies - enzymatic, chemical, steam - which do not add cost limitations to what ultimately must be an economically competitive overall process.

Here are some figures to contemplate: conversion of existing annual stocks of corn and sugarcane (or other) crop-based fermentable carbohydrates to bioethanol can 'buy' up to 6% of the present U.S. demand for transportation fuel. To make a bigger dent in the transportation fuel supply, the cellulosic component of plants must be brought into play. On a successful commercial scale, cellulosic ethanol, can potentially provide 20% or more of the U.S. current demand for transportation fuel. Thus the 'rush to production' of cellulosic ethanol is on, converting both readily fermentable carbohydrates (sugars, starch) as well as cellulosic material to a product mix from which ethanol can be isolated and purified, then added to e.g. gasoline to produce a blend containing 10% ethanol (E-10) or higher, even to pure ethanol.

To carry out conversion of the cellulosic and hemicellulosics to ethanol, or to recover energy from lignin, or to produce fuels other than ethanol (eg. biobutanol, hydrogen) or to use thermal methods (eg. pyrolysis, gasification) to produce either gas ('syngas'), or combustible liquids (by eg Fischer Tropsch synthesis), or to co-produce non-fuel byproducts (solvents, monomers, biopolymers) as part of the overall biomass to energy biorefinery, will require chemistry, and inter/multi-disciplinary science in which chemistry is a significant component. Agricultural chemists can immediately contribute in such areas as feedstock characterization, including of details of plant cell wall chemical architecture, in following the course of fermentations, in separation of components/products of biorefining, and in converting byproducts such as lignin and glycerol to more useful end-products. For both biodiesel and bioethanol fuels, chemistry can help in selecting and modifying promising feedstocks, in the latter case through delineating biosynthetic pathways, and with molecular geneticists, modifying

or engineering pathways to optimize production of better feedstocks. Natural product chemists can discover new plant, animal, or algal sources of hydrocarbons (eg high in wax, terpenes, sterols or other reduced photosynthesis-derived fuel or fuel precursors). Chemistry and chemical engineering will contribute to developing the biorefineries themselves, ideally producing a range of potential products - fuels, lubricants, chemical building blocks, - as do today's generation of petroleum refineries but with added possibilities of producing soil amendments, food/feed, fibers, building materials, etc. and other bio-based products. Further downstream conversion products might include solvents, monomers, food and feed ingredients and a host of other useful chemicals and mixtures. Chemistry can also contribute to solving existing problems associated with present-day energy sources, such as carbon dioxide removal from source effluent or even the atmosphere itself, removal or mitigation of other transportation associated pollutants from air, water, and soil, and development of new analytical methods for certifying new feedstocks, fuels, and fuel blends as well as the inevitable mix of byproduct contaminants which is often associated with new alternative technologies.

The new bioeconomy will offer many opportunities for agricultural chemists and agricultural scientists in general and may afford one of the biggest opportunities - for research, international interdisciplinary collaboration, development of new college and university level courses and curricula, and influencing public policy - to appear on the scene for some time. Some of this work will affect the content of the *Journal of the Brazilian Chemical Society* and *Journal of Agricultural and Food Chemistry* and likely a host of other Journals, some of which are yet to be launched. It is timely that Brazil and the U.S. are already cooperating on several bioenergy fronts [See *Chemical and Engineering News* **2007**, 85,15] and are so well positioned to take advantage of these opportunities. Attending the 2007 national meeting of the Brazilian Chemical Society gave me an opportunity to hear about research first-hand. I was highly impressed with the creativity of Brazilian scientists which, no doubt, has been a major contributor to the rapid development of biofuel and bioenergy technology in Brazil.

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