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SYMPOSIA

Biorefineries– A Path to Sustainability?

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ABSTRACT

Biorefining of crops for production of power, transport fuels, and a diverse array of chemicals has potential for providing significant added economic value to biomass. A shift in the industrial resource base from fossil resources to biomass also requires a shift in the technology base for producing, handling, and processing of raw materials. Biotechnology will play an important role in providing tools for different stages ranging from biomass production, treatment, and valorization to various products. First generation refineries have raised some critical issues related to land use and insufficient environmental benefits due to energy-intensive cultivation of crops. The abundant residual lignocellulosic biomass will constitute an important feedstock for the future biorefineries so as to have a minimal impact on the food availability. Necessary investments in technological development will be needed to realize the benefits of the new bioeconomy in the long term.

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The 20th century has been an era of petro-chemistry that has provided society not only with energy, but with vast numbers of other products that have influenced almost every facet of modern life. A tremendous increase in energy demand—over 50% by 2025—is projected, with much of the demand emerging from the rapidly developing nations (Ragauskas et al., 2006). There is a growing concern, on the one hand, for the dwindling supply of fossil resources and high energy prices, and, on the other hand, for the deleterious consequences of climate change related primarily to greenhouse gas emissions from the burning of fossil oil and unsustainable means of production. This has triggered a global development toward shifting the dependence from fossil to alternative cleaner renewable resources. The 21st century has started with a promise to open up new avenues for increasing the use of renewable resources in the global economy.

A major part (up to 90%) of fossil oil is used for the production of power, heat, and transport fuel, while only a few percent in the form of naphtha finds its way for the manufacture of chemicals and materials (U.S. Department of Energy, 2006). The latter, however, accounts for an impressive added economic value—close to half of that generated by the petroleum industry. While a number of renewable options, namely solar, wind, hydroelectric, and biomass, are available for the generation of electricity and heat, biomass is the only current renewable source that can be used for the production of liquid and gaseous transport

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fuel, as well as for chemicals and materials. Hence, when moving from a fossil- to a bio-based economy, integrated production of chemicals and materials with that of bioenergy is essential to maximize the value generated besides minimizing the carbon footprint.

BIOMASS-BASED REFINERIES

Plant matter constitutes the most abundant source of biomass on earth and is produced through photosynthesis. The number and variety of products that have been based on biomass during the petrochemical era are rather modest. These include mainly natural fibers and other natural products used in paints, soaps, adhesives, lubricants, inks, polymers and resins, and in the production of several antibiotics, drugs, amino acids, etc. Currently, the largest bio-based products are the biofuels. A shift in the industrial resource base from fossil to biomass will require development of effective biorefinery systems, analogous to petroleum refineries, centered on an agricultural or forest base. In this case the biomass is separated into different fractions for production of transport fuel, electricity, and various chemicals. The commercialization of the biorefineries will be determined by exploitation of the full potential of the biomass to utilize the spectrum of complex organic macromolecules (carbohydrates, oils, proteins, and lignin) and also other chemical constituents such as antioxidants and pigments present therein. Exploiting each one of these components would lead to the production of a multitude of products ranging from high volume-low market value to a low volume-high market value. These include commodity products, such as biofuels and biomaterials, platform chemicals (such as lactic acid and succinic acid), specialty chemicals (such as biosurfactants and biolubricants), and fine chemicals. Maximizing the usage of biomass will also lead to the improvement of process economics and waste minimization (Koutinas et al., 2007).

Viewed from a different perspective, replacement of petroleum by biomass feedstocks would reduce the dependence on imported nonrenewable petroleum, the supply of which is normally governed by political, economic, and ecological factors. Utilization of domestically produced biomass would provide markets and increased net income for the agriculture/forestry sectors and also more employment opportunities. This trend will potentially provide new opportunities for developing countries and lead to better use of their resources and reduced impact on the environment.

TECHNOLOGIES FOR BIOREFINERIES

Due to the differences in the nature and composition of fossil- and biological feedstock, a shift in the technology base is needed. A combination of physical, chemical, and biological processing technologies is foreseen for producing, handling, and processing of raw materials. Biotechnology will play an important role in providing tools for different stages of a biorefinery starting from feedstock development, hydrolysis of complex biomass components to simpler molecules, and the production of biofuels and chemicals. The possibility to use both traditional breeding and molecular biology techniques for increasing yield performance of plants, and to alter their composition, has no parallel in petroleum refining. Improvement, with regard to biomass production, could involve development of tailored perennial plants. This might include desirable physical and chemical traits such as increased concentrations of a certain component, increased resistance to drought and pathogens, and reduced fertilizer needs. Increasing the biomass yield may be achieved by the manipulation of photosynthesis to increase the initial capture of light energy that, at present, is less than 2%, and by extending the growth phase of plants, and by manipulating nitrogen metabolism (Ragauskas et al., 2006). Development of genetically engineered microorganisms will be needed for improving fermentation productivity and minimizing formation of by-products during the fermentation process in the production of biofuels and chemicals. Access to efficient and stable enzymes will allow energy-efficient biomass treatment and chemical production.

The technologies for initial processing of biomass should, ideally, be such that they can be adapted to differences in the quality of the raw material from different crops. As biomass can contain large amounts of water and is also sensitive to environmental conditions, efficient means to reduce the water content and convert the feedstock to a form that is stable during storage under ambient conditions before further processing will be needed. Furthermore, improvements in some existing process technologies, in terms of energy efficiency and yields, and for recycling of wastes, are desirable for a successful biorefining.

FIRST GENERATION BIOREFINERIES

A first generation of fuels (ethanol and biodiesel) and chemicals (polylactic acid) is currently produced from starch-, sugar-, and vegetable oil-feedstocks. Bioethanol is produced from sugarcane (*Saccharum* spp. L.) or corn (*Zea mays* L.), and biodiesel from soybean [*Glycine max* (L.) Merr.], rapeseed (*Brassica* spp.), or palm (*Cocos nucifera* L.) oil. Although an enormous expansion of the biofuel market has occurred exceeding an estimated 53 billion L in 2007, these biorefinery operations are not yet designed to make optimal use of biomass, minimize energy input, recycle wastes, and to generate good net income (Koutinas et al., 2007). No valuable components have been isolated and the residual by-products are mainly used as low-cost animal feed or in foods and in some cases for providing process energy. An important by-product of the biodiesel, as well as ethanol production, is glycerol, which has the potential to be used as a platform for a number of specialty and high-value chemicals (Werpy and Petersen, 2004).

The biorefineries based on agricultural crops have furthermore raised some critical social and ecological issues. They compete with food for the feedstock and the land used for growing the crop. Due to increased demand for biofuel production, the annual increase in grain consumption since 2005 has risen from 20 million to 50 million t (Bourne, 2009). Diverting the crops for biofuel production is seen as an important factor underlying the drastic increase in food costs during 2008. Increasing demand for food, feed, and biofuels has also been a major cause of deforestation in the tropics; Brazil alone increased its soybean plantations in the Amazon 10% a year from 1990 to 2005 (Bourne, 2009). Yet another important fact is that potential savings in CO_2 emission and fossil fuel consumption has been compensated for by the energy-intensive cultivation and processing of the crops. The use of significant amounts of nitrogen fertilizer, herbicides, and pesticides during cultivation of corn further contributes to ground and river water pollution (Pimentel and Patzek, 2005).

THE FUTURE BIOREFINERIES

The existing biorefineries will continue to grow and their future development will be geared toward increased sustainability by maximizing the utilization of biomass, improving energy efficiency, and being less wasteful. For new biorefineries the selection of suitable biomass resources is extremely critical for them to operate in symbiosis, rather than in competition, with the food sector and other markets (e.g., those based on forestry). Further, biomass resources should have an ecological perspective regarding the minimal need for water, fertilizers, and other resources for its production. In some countries, biorefineries are being fueled by alternative crops such as sweet sorghum [*Sorghum bicolor* (L.) Moench] and Jerusalem artichoke (*Helianthus tuberosus* L.; JA), which are fast growing under varying climatic conditions with low water/chemicals input and are expected to provide good economies in the long term (Peters, 2006; Grassi and Sénéchal, 2007). The latter is able to grow in saline and desert areas and is not used for human consumption, since its main polysaccharide, inulin (a fructose polymer), is not easily digested.

In general, the ideal feedstock for a biorefinery is considered to be the residual organic by-products accumulated in abundance and with low or no profit and nutritional value. These include agricultural food and feed crop residues, wood and wood wastes and residues, grasses, dedicated energy crops and trees, plants (including aquatic plants), animal wastes, municipal wastes, and agricultural or industrial waste streams. Examples of the agricultural byproducts are wheat (*Triticum aestiwm* L.) and rice (*Oryza sativa* L.) straw, sugarcane bagasse, corn stalks, and soybean residues, whereas large industrial waste streams originate from paper making, food processing, and even the biofuel industry. Among the dedicated crops, short chain woody crops such as willow (*Salix* spp.) and eucalyptus (*Eucalyptus globulus*), and herbaceous plants, e.g., perennial grasses like switchgrass (*Panicum virgatum* L.) and bermudagrass (*Cynodon dactylon* [L.] Pets.), are considered to be the most promising source of biomass for energy production (McKendry, 2002; Keoleian and Volk, 2005).

The common feature of the above biomass materials is that they are lignocellulosic in composition and their global production is estimated at 3 to 5 Gt/yr, which represents 10 to 20% of today's world energy demand (Lange, 2007). They are available at a fraction (one-fifth to one half) of petroleum costs on an energy basis. Rice straw, wheat straw, bagasse, and corn stover are the major residues generated in developing countries (Dale and Kim, 2006). Over 700×10^9 kg of rice straw is produced worldwide, mostly in Asia and much of it is burned in the fields. Almost 200×10^9 kg bagasse is collected annually and is used as a low-cost fuel in the sugar industry. The possibility to use such abundant and inexpensive residual materials as feedstocks will also result in greater net savings in energy and CO_2 emissions as energy for cultivation need not be accounted for, as it has been already recovered from the land.

The main bottleneck for the use of lignocellulosics, in contrast to starch and sucrose, is its recalcitrant nature, necessitating feedstock pretreatment to get access to the components. About 65 to 85% of the lignocellulose is made of cellulose and hemicellulose that acts as supporting or scaffold structures in plants (Kamm et al., 2006). Cellulose is the predominant polysaccharide with a non-branched crystalline structure composed of glucose residues, while hemicelluloses occur in close association with cellulose and constitute an average of about 20 to 30% of the biomass. They are heterogeneous, branched polysaccharides containing C_5 sugars (like xylose, arabinose) along with C6 sugars and sugar acids. Lignin accounts for 10 to 20% of the lignocellulosic material. It is covalently associated with hemicellulose and forms a permanent bonding agent between cellulose fibers in plants. Efficient and cost-effective separation of these components will lead to a breakthrough in biorefinery development.

INTEGRATING ENERGY AND CHEMICALS PRODUCTION

Some alternative approaches are possible for co-production of energy and chemicals from biomass. One frequently advocated technology is gasification of biomass to syngas (a mixture of H_2, CO, CO_2, CH_4, and N_2) which can be used as a platform for production of hydrogen and synthetic gasoline as fuels, and of methane and methanol as building blocks for a large number of chemicals. Such a technology is less sensitive to specific substrates converting it into the simplest forms irrespective of inherent energy. The other approach is to separate and utilize different components of the biomass individually for production of bioenergy and chemicals.

Two routes can be followed for using biomass feedstock for the chemical industry. One is to follow the structure of the petrochemical industry by manufacturing a set of platform chemicals that serve as building blocks for secondary products, which in turn can be used to form other products for different applications. The other route is to target new chemicals that provide environmentally benign substitutes for the current petrochemicals. It is claimed that many of the chemical building blocks that are obtained today from fossil resources can also be produced from biological feedstocks (Werpy and Petersen, 2004; Frost, 2005; Christensen et al., 2008).

Oil feedstocks have been and will remain important raw materials for specialty products like polymers, biolubricants, biosurfactants, and emulsifiers, in addition to biodiesel. However, due to their sheer abundance, carbohydrates are the natural choice as feedstock for biorefinery development. The coming years will see considerable development in process technologies for energy and chemical production from carbohydrates. The most abundant sugar, glucose, is the key basic chemical around which a complex biorefinery network will evolve. Glucose is currently obtained from starch, but it will potentially be available from cellulose once the technology for its hydrolysis is developed. Among the important processes are microbial fermentations for conversion of glucose and other sugars to a large number of products. These include energy carriers like ethanol and butanol, organic acids, such as lactic acid, succinic acid, and itaconic acid, bioplastics, such as polyhydroxyalkanoates, etc. The fermentation residues are often used as animal feed, but could be subjected to anaerobic digestion to produce biogas that can be used for heating or as a gaseous transport fuel. The availability of ethanol makes it interesting for use as a platform for producing several bulk chemicals like ethylene, acetic acid, and butadiene. Ethylene, in turn, can be used as a raw material for benzene, toluene, and xylene production. Organic acids, on the other hand, are good precursors for polymers, solvents, etc.

A variety of chemical technologies are available for upgrading the sugars to different product groups with broad application potential. Examples are hydrogenation of sugars to C5–C6 polyols (e.g., xylitol, mannitol, and sorbitol) and hydrogenolysis to C2–C3 glycols, e.g., ethylene and propylene glycol. Acid-catalyzed dehydration of hexoses yields 5-hydroxymethylfurfural (HMF) and levulinic acid, and of pentoses to furfurals, which provide economic routes to furfural and furan chemistry and a variety of polymers (e.g., nylon, polyalcohols, polyesters, polyamides, and furan resins [Werpy and Petersen, 2004]). Some of the other promising product lines that can be developed from sugars are pyran building blocks, unsaturated *N*-heterocycles, and aromatic chemicals, which are potential precursors for fine chemicals and pharmaceuticals. Enzymatic catalysis may also be used to catalyze specific reactions at the different positions of sugars.

With future development of biorefineries to process lignocellulosic feedstocks, the amount of lignin potentially available for conversion into value-added products, rather than its fuel value, will be enormous. The partially hydrolyzed lignin has excellent properties for use as substitutes for phenol-formaldehyde resins, polyurethane foams, adhesives, insulation materials, rubber processing, antioxidants, and dispersants for dyes, herbicides, pesticides, and fungicides. It provides a cheap source for high-value products like vanillin and syringol for the flavor and fragrance industry, and syringaldehyde for use as hair and fiber dye, as well as a pharmaceutical precursor (Eckert et al., 2007). Some potentially interesting new markets for lignin are the production of printed circuit boards for the electronics industry and low cost carbon fibers for use in automobile and light truck body components (Pye, 2006).

A variety of other relatively minor components of lignocellulosics, such as proteins, terpenic oils, fatty acids/esters, and inorganic materials, will also become available for different markets. For example, the amount of protein generated will be much greater than that required for meeting the nutritional requirements of the human population. In addition to their conventional application as animal feed, protein residues can target other end uses including nutrient additives for microbial fermentations and use of amino acids as building blocks for functionalized chemicals such as amines (Sanders et al., 2007).

THE NEW BIOECONOMY AND THE DEVELOPING COUNTRIES

Biorefineries for integrated production of bioenergy, chemicals, and materials hold promise for both short- and long-term sustainability for developing countries. Among the most successful examples of first generation biorefineries occurred in Brazil, which is leading worldwide in the production of ethanol, providing some 18% of the country's automotive fuel. As the use of biomass and implementation of biorefineries will increase with time, the concern with providing food as well as bioproducts, while maintaining productive soils and effective infrastructure, will become more and more important.

Increasing food prices over the years indicates a relatively stagnant agricultural productivity that cannot satisfy the increasing consumption trends of neither a growing population nor an increasing prosperity in countries like China and India (Bourne, 2009). Several countries face deteriorating farming conditions as a consequence of agricultural practices involving overuse of fertilizers, pesticides, and irrigation, and removal of all crop residues from the fields. This has resulted in increased salinization and water logging of soils, and contamination of ground water. The increasing threat of climate change—with hotter seasons and increased water scarcity—is projected to reduce future harvests in many parts of the world. Better farming practices to maintain productive soils and crops with the desirable traits are thus needed to cope with the demands of the growing population as well as to sustain the bioeconomy.

Establishment of the petrochemical industry has been supported by the development of an effective infrastructure of petroleum refineries, and transport and distribution network with low production costs. There is a similar requirement to obtain the maximum value from bio-based production. The limiting factors here are that the biomass feedstocks are generated discontinuously, are perishable, and require large transport volumes (Narodoslawsky et al., 2008). In many developing countries, it is very difficult to organize a good raw material supply because of poor roads and storage infrastructure, and also little incentives for farmers to improve their yields. Initial processing of biomass on a small scale close to the harvest location has been proposed to coincide with its production and would provide benefits in terms of minimal transportation, better recycling of minerals, new forms of integration in energy utilization, and labor organization (Sanders et al., 2007). Production of an intermediate product containing less water and a better shelf life could be transported to larger processing plants and would enable production throughout the year, leading to lower capital and labor costs and better prices for by-products. This would potentially give a higher return to the farmers.

To take advantage of the potential existing in the locally produced biomass, a major challenge for the developing countries will be to participate in technology development and application. This would include both improving the biomass productivity and subsequent valorization of the biomass.

CONCLUSIONS

Biorefining of crops into multiple products, including energy, chemicals, and materials, will increase the overall value of biomass. The maximum potential of the biorefinery will be realized by advances in biotechnology, plant genetics, separation technologies, process chemistry, and engineering. To be sustainable, and also to avoid increases in the raw material prices, the future biorefineries would have to concentrate on lower quality renewables such as grasses, harvest residues from crops, by-products, and wastes from the food industry, forestry, or society. Furthermore, recycling of waste would be needed to make the entire process carbon-neutral. As in other technological fields, participation in the new bioeconomy will be uneven and limited to those countries that make the necessary investments in technological development.

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