

SESSION 1: Fine chemicals, biologically active products and commodities from wood components

A REVIEW OF BIOMASS AS THE NEW FEEDSTOCK FOR THE MATERIAL AND ENERGY NEEDS OF THE 21ST CENTURY

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Abstract

A large percentage (nearly 100 million metric tones) of organic chemicals produced annually in the United States is petroleum in origin. The potential environmental pollution loading during use and the end-of-life cycle criteria such as disposal, pollution, and degradation are therefore enormous and merit innovation and change to offset environmental impacts. Therefore, diminishing pollution caused by petrochemicals is propelling the green technologies which are becoming more attractive as witnessed by the significant attention bioethanol is receiving. It is inarguable that the dwindling hydrocarbon economy will become unsustainable while the cost of crude oil continues to increase, and agricultural products see dramatic decreases in world market prices. These trends provide bases for renewed interest in the use of biomass as a feedstock for the development of a carbohydrate-based economy as the logical alternative to fossil fuel resources. This proceeding will provide an overview of the green revolution and serve as a springboard for discussion of the new chemicals, materials, and energy paradigm that is receiving much attention recently.

Introduction

Petroleum is the most important *fossil fuel*, a class of fuels that are non-replenishable, geological resources, the so-called "biomass of earlier eras" (1). Petroleum is indispensable; however, since the energy crises thirty years ago, we realize that it is a finite resource. Fifty years ago, Hubbert predicted a maximum peak for the oil production whose timing ominously coincides with current increasing petroleum prices.

The National Renewable Energy Laboratory defines biomass as organic matter available on a renewable basis (2). Biomass includes forest and mill residues, agricultural crops and wastes, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, fast-growing trees and plants, and municipal and industrial wastes. In general, biomass can include anything that is not a fossil fuel, but is bio-based.

Biomass provides a naturally abundant resource that is sustainable. The bioindustry presents an environmentally friendly alternative to the petroleum industry. The productive use of waste residues allows for lower emissions to the atmosphere, since CO₂ from biomass is considered neutral, and could provide a new source of economic growth for rural communities. Presently, the available biomass resources could provide as much as 6-10 quadrillion BTU of feedstock energy, corresponding to the energy required to manufacture over 300 billion pounds of organic chemicals (2).

The thousands of different industrial bioproducts produced today can be considered as stemming from sugar and starch, oils and lipids, gum, wood and finally cellulose (2, 3, 4, 5, 6).

Annual production of industrial corn starch products is estimated at 6500 million pounds, which corresponds to an estimated value of 2200 million dollars. Industrial ethanol production is estimated at 3.41 billion pounds. Oil- and lipid-based bioproducts include fatty acids and oils derived from soybeans, rapeseed, and other oilseeds. 400 million pounds of glycerine are produced annually. Over 1200 million pounds of soy oil, peppermint, spearmint and other plant oils are also produced annually. Gum and wood chemicals include tall oil, alkyd resins, rosins, pitch, fatty acids, turpentine, and other chemicals derived from trees. The annual production of these is approximately 3200 million pounds per year. Cellulose derivatives, fibers and plastics include products such as cellulose acetate (cellophane) and triacetate, cellulose nitrate, alkali cellulose, and regenerated cellulose. The primary sources of cellulose are bleached wood pulp and cotton linters. Cellulose derivatives have an annual production of 2140 million pounds.

The use of biomass for energy, materials and chemicals parallels the concept of the biorefinery. A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, heat and high-value chemicals from biomass. Byproducts, residues and a portion of the produced fuels are used to fuel the biorefinery itself. A biorefinery may produce transportation fuels (low-value product) in high volumes, high-value chemicals in low volumes, while generating electricity and process heat for its own use and perhaps surplus for sale into the power grid. The high-value products enhance profitability, the high-volume fuel helps meet national energy needs, and the power production reduces costs and avoids greenhouse-gas emissions.

Results and discussion

Bio-Based Chemicals

Cellulosic biomass from plants can be a raw source of sugars for industrial processes. The use of this biomaterial presents several advantages. Theoretically, cellulose is a less expensive feedstock than petroleum. Moreover, its use would not affect food supplies, and chemicals derived from lignocellulosics would have a lower impact on the environment than petrochemicals. Additionally, cellulosic biomass is considered carbon dioxide neutral, since its burning does not add any carbon to the atmosphere, beyond what was required for the plant to grow. This makes it a "green", environmentally friendly alternative to fossil fuels.

Presently, only five percent of all global chemical sales relate to "green" products, derived from natural resources. Nevertheless, this market share has the potential to rise as high as 20% by 2010 and may reach 2/3 of the total global economy, if technological advances, low-cost enzymes and new recombinant technologies are made available on a large scale. Consequently, the potential benefits of a "bio-industry" are enormous and alternate bio-based routes for the synthesis of traditionally petrochemically derived products should be carefully examined.

The Pacific Northwest National Laboratory took part in a collaborative study with the National Renewable Energy Laboratory in an effort to identify the top-tier building block chemicals for biorefineries (7). The top twelve chemicals (Figure 1) were selected based on their compatibility with existing petrochemical processing as well as their ease of synthesis. The compounds are: 1,4 diacids (succinic, fumaric and malic), 2,5 furandicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol/arabinitol. These molecules have six to twelve carbon atoms and multiple functional groups.

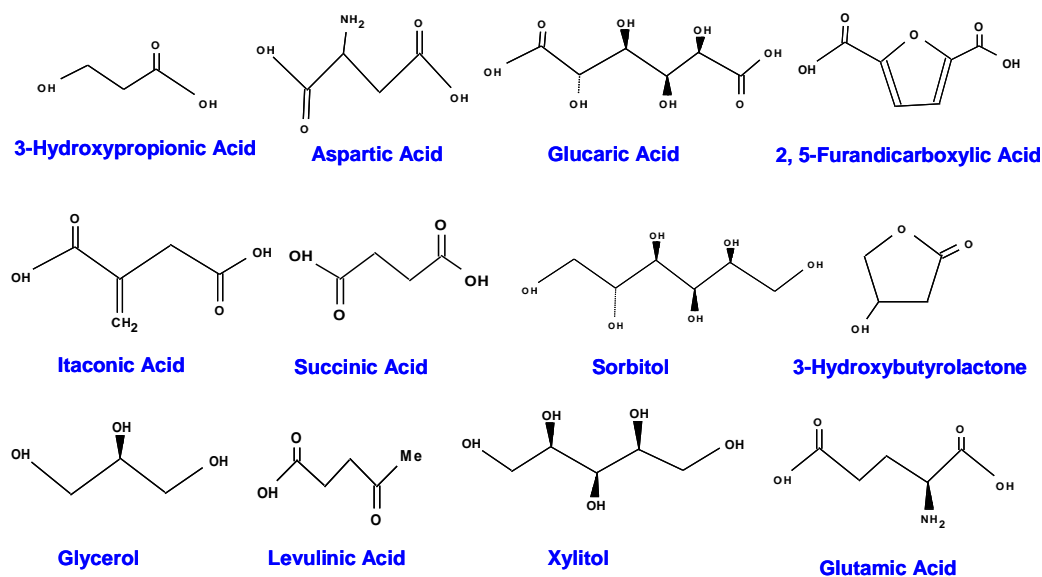


Figure 1. Chemical building blocks from biomass compatible with existing petrochemicals.

As opposed to many synthetic chemicals, forest-based and agricultural biomaterials are readily renewable, inexpensive, and environmentally benign. Despite a significant amount of recent research for augmenting the industrial use of readily available carbohydrates as raw materials (8,9,10,11,12,13) (e.g., car moldings, cosmetics, food and additives), the systematic exploitation of this vast resource, as already indicated, is still in its infancy. Since clean air pressures are mounting while the availability of cheap and abundant fossil fuel becomes increasingly questionable as seen in the current climate, it is likely that any economic advantages for a petrochemical-based economy will evaporate within the next fifty years.

For example, DuPont Company (USA) has determined that once the price point at which an extractive from plants, tulapilin (A- α -methylenebutyrolactone) shown in Figure 2, becomes competitive with its commercial analogue, methyl methacrylate (MM), the natural material will be used commercially for polymer applications (14). MM is a feedstock that is used for polymerization to manufacture a number of plastics, moldings, and related materials. Its natural analogue, tulapilin A, produces a polymer whose durability and refractive index rival that of MM (14). Remarkably, DuPont has also found that limonene, a citrus tree extractive, mimics the chemistry of 4-vinyl-1-cyclohexene in that it can be used as an anchoring point for the introduction of alkoxy-silanes for exterior coatings (14).

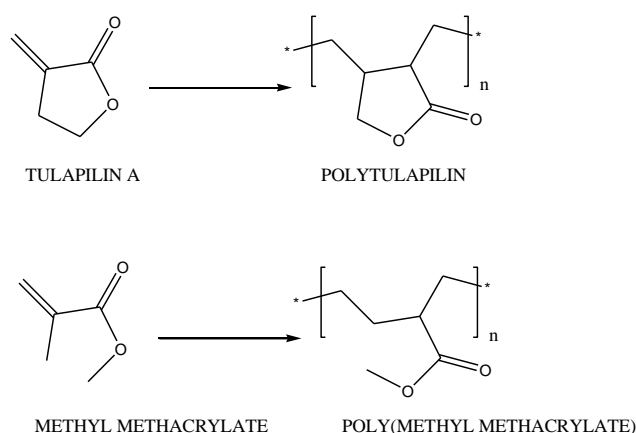


Figure 2. Shown above in the top structure is the natural product extract, tulapilin A (A- α -methylenebutyrolactone), found in tulips, and below it is its synthetic analogue, methyl methacrylate. Notice the strong chemical structural similarity in both the monomer and polymer.

An early example of a bio-based “green” solvent is a new class of chiral ionic liquids that can be derived from α -pinene, an extractive from pine trees, as shown in Figure 3. Ionic liquids are salts that are liquid at or near room temperature. As such, they are composed of an anion and a cation, like any salt, but they do not have the high melting points typical of such species. Since the combination of organic cations and anions is virtually limitless, several classes of ionic liquids have actually been reported with more and more such systems discovered continuously.

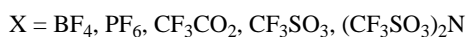
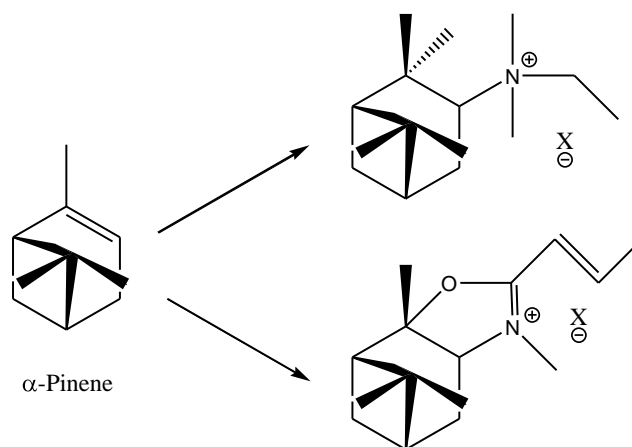


Figure 3. Structure of α -pinene, a natural extractive from pine trees, which can be converted to two distinct chiral ionic liquids.

Bio-Based Energy

Heating & Steam. Biomass has been used since the early ages of humanity as a source of energy, principally heating. Nowadays, new developing energy technologies are broadening its use well beyond simple combustion for heating. The conversion processes used on biomass feedstock allow the generation of steam and electric power, as well as, a wide range of energy products such as, ethanol, biodiesel, fuel gas and chemical intermediates and products. The conversion of biomass feedstock into energy products are well established technologies, with enhanced improvements in the last decades. This subject has been previously reviewed (15).

Biomass has been used for simple heating by direct combustion, which by nature is a very low efficient operation (approximately 7% in an open fireplace and 15% in a fireplace with convective tubes) (16). Efficiency improvements are realized by larger scale combustion processes in boilers or furnace, thus improving heat recovery and therefore overall efficiency.

Boiler applications further provide the opportunity to generate electricity power from the incoming biomass. The biomass is burned to generate steam, which is then used to turn a turbine for the generation of electric power. The majority of the biomass-based power plants are found in the pulp and paper industry. Woody residues from the wood raw material and the black liquor, as a by-product from the pulping process, are consumed in order to generate the necessary power for the plant operations. When black liquor is burned for energy recovery, the pulping chemicals are recovered and recycled, thus further reducing the costs.

Biomass based Combined Heat and Power (CHP) systems provide the primary energy for large segments of the population in many European countries, mainly Scandinavian and northern countries. These systems, typically combust biomass to produce high pressure steam for further electric power generation. Lower pressure steam is then extracted from the turbine system and used for district heating.

Ethanol. Ethanol production is known for alcoholic beverages such as wines and beers. It is produced through natural fermentation of the starch and sugars present in different biomass forms by biological organisms. Currently, grains of wheat or corn are typically the primary source for the production of ethanol as fuel, which can be blended with other fuels, as gasoline (17,18). Other sources for ethanol production, which are also used are straw, sugar cane, sugar beet, and wood (19).

Large-scale production of ethanol makes use of fermentation process as well. In a first stage, biomass material, such as corn kernel or other starchy grain, is milled through a dry or wet milling mode. The fermentation then takes place by mixing the resulting flour (polysaccharides) in water with yeast. The mixture is heated at 30°C to initiate the fermentation reactions, under an anaerobic environment, and takes 1–2 days for completion. After fermentation, the ethanol is filtered and then distilled to increase its concentration from 10 to 95%. The concentrated ethanol is then blended with petroleum-based fuels to the desired concentration.

Ethanol can also be produced from cellulosic biomass such as agricultural residues, forestry residues, waste paper, yard wastes, portions of municipal residues and industrial residues (20). The long-chain polysaccharide materials are initially treated with acid or enzymes to cleave the glycosidic bonds. The acid recovery system can be a complex process. Research is being performed in order to find ways to reduce the acid levels while maintaining high conversion levels. The resulting small fractions can then readily be fermented to ethanol. In parallel, small fractions of biomass can be used to grow fungi and other organisms to produce enzymes (cellulase), which hydrolyze cellulose to glucose. Figure 4 presents a scheme for the production of ethanol from cellulosic biomass (20). There are a variety of and several technologies combine two or all three of the hydrolysis and fermentation steps within the shaded box.

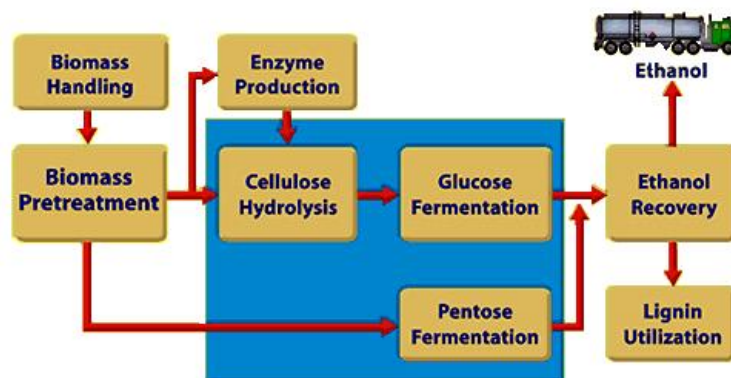


Figure 4. Basic steps in production of ethanol from cellulosic biomass (20).

U.S. ethanol production has grown significantly in recent years. In 2004, a record 3.41 billion gallons of ethanol were produced — an incredible 109 percent from 2000 (21). But ethanol plants do not make only ethanol. Depending on the type of facility, a number of other coproducts result from ethanol production, adding even more value to corn feedstocks and to the economy. Dry mill facilities also produce distillers dried grain with solubles (DDGS) and carbon dioxide. Ethanol wet mills can also produce corn gluten meal, corn gluten feed, sweeteners and corn oil. These coproducts and byproducts from cellulosic biomass ethanol production can be used to produce value-added chemicals, contributing to the economy of fuel production from biomass. On the other hand, ethanol can also be used as a chemical intermediate in the production of other organic chemicals.

Oxygenated transportation fuels, as the ethanol-gasoline blends, can benefit environmental conditions. Mixtures of up to 10% ethanol referred to as (E10) can be utilized in most gasoline designed engines with no modification. More concentrated blends, namely, the E85 and E95 blends (85 and 95% ethanol, respectively) require specifically designed engines, referred to as “flexible fuel” engines to perform properly. These flexible fuel engines can run on either gasoline or

high concentration ethanol blends. Automobile manufacturers are producing more vehicles that can use these high ethanol blends each year, thus increasing demand. The spark ignitions, Otto-cycle engines used in today's automobiles, even in their early stages of development, were designed to operate with ethanol containing fuels. Henry Ford designed the early Model T to use ethanol as a major fuel source. Such plans were changed subsequently when storage and transportation difficulties combined with high corn prices at the time caused the supply of ethanol containing blends to be reduced.

Biodiesel. Biodiesel is a fuel that can be made from renewable resources such as vegetable oils or animal fats. It is usually produced from soy or canola oil. Other possible resources are recycled fryer oils. Through a transesterification process, the oils are converted into the biodiesel. The latter can be used as pure fuel or blended at any level with petro-diesel, by diesel engines. Biodiesel is designated B100 and meets the requirements of ASTM (American Society for Testing & Materials) D 6751.

Biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. A lipid transesterification reaction is used to convert the base oil to the desired biodiesel. The most common process uses methanol to produce methyl esters, although ethanol can also be used to produce an ethyl ester biodiesel. In the production of biodiesel, the triglycerides in the oils and fats are reacted with methanol (or ethanol) to make methyl esters (or ethyl esters) and glycerol, as a byproduct. The process uses a catalyst, typically NaOH or KOH to enhance the reaction rates. Some oils may have to undergo some pretreatment before reaction with methanol, to avoid the formation of high concentrations of free fatty acids. The reactions take place at low temperatures (65°C) and at modest pressures (2 atm). Biodiesel is further purified by washing and evaporation to remove any remaining methanol. The oil (87%), alcohol (9%) and catalyst (1%) are the inputs in the production of biodiesel (86%), the main output. Other byproducts include glycerine (9%), alcohol (4%) and fertilizer (1%). Nothing is wasted in biodiesel production (22).

Biodiesel can be a direct substitute for petro-diesel, either as neat fuel (B100 or BD 100) or as an oxygenate additive at any concentration blended with diesel. Typically, the biodiesel that is primarily utilized is the B20 blend (20% of biodiesel and 80% of petro-diesel). Pure biodiesel or blends can be used in any compression ignition (diesel) engines. B20 earns credits for alternative fuel under the US Energy Policy Act of 1992. Ranges as low as 2% (BD2 or B2), have been shown lubricity benefits (23). In 2004 almost 30 million gallons of commercially produced biodiesel were sold in the U.S., up from less than 0.5 million gallons in 1999 (24). Due to increasing pollution control requirements and tax relief, the U.S. market is expected to grow to 1 or 2 billion gallons by 2010.

Rudolf Diesel had successively presented an engine powered by peanut oil (biofuel) at the World Fair in Paris, France in 1900, where he received the "Grand Prix" (highest prize). He believed that the utilization of biomass fuel was the real future of this engine. In a prophetic 1912 speech, Rudolf Diesel said, "the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time." (25).

Conclusions

In retrospect, the petroleum age has served the growth of civilization well. However, it has also become an albatross to further growth because of its basic deficiencies in environmental compatibility, sustainability, and micro- and macroeconomics. As Rudolph Diesel so astutely intimated, we are now at the nexus of a major crossroads in the future of humanity with respect to the production of chemicals, materials, and energy. The only real solution which is viable is the efficient and intelligent use of biomass. Capturing the chemical and material value of biomass will provide the world with a vast window of freedom from the economic and geopolitical uncertainties associated with petroleum dependency. In addition, tapping into bio-based fuel sources such as ethanol and diesel expands that horizon considerably by supporting environmental stewardship by their renewable nature and carbon neutrality.

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Acknowledgements

We gratefully acknowledge the support of the US Department of Energy (Cooperative Agreement No. DE-FC36-01GO10626) and the USDA (Cooperative Agreement No. 2006-38411-17035 (Higher Education Challenge) for partial support of this work.