Materials, Chemicals and Energy from Forest Biomass

MATERIALS, CHEMICALS AND ENERGY FROM FOREST BIOMASS
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This book will explore our forests as the most readily available and renewable source of carbon as well as the building block of chemicals, plastics, and pharmaceuticals as the next 100 years gradually push consumers toward alternate sources of chemicals. Meeting these needs from trees requires that new chemistry be developed so that plant material is converted to commodity chemicals. This focused discussion on ongoing global efforts at creativity using forest and biomass based renewable materials will include different mechanisms for bringing about change on this very innovative topic.

Despite the fact that the material emerged from a symposium, it is not a collection of fragmented research findings in the form of conference proceedings. Most chapter contributors attempted to provide a good review of the literature, creating a sound foundation for the science to be subsequently developed. Furthermore, a collection of authoritative reviews is also provided at the onset of the book prior to embarking on specific topics.

Without a doubt, (to quote the editor from his introductory observations 'our society's concerns over increasing fuel prices, green house gas emissions, and the associated global warming have created a tremendous interest in the science and technologies that promise the sustainable production of materials, chemicals, and energy from domestic resources. In this respect, lignocellulosic biomass has the unique ability to supply all of the above because carbohydrates and lignin are among the most abundant organic compounds on the planet, representing a vast amount of biomass (in the range of hundreds of billions of tons). It is interesting to note that only 3% of this vast resource is actually used by humans. Despite the fact that a significant amount of research has been carried out aimed at augmenting the industrial use of readily available carbohydrates as organic raw materials, the systematic exploitation of this vast resource is still in its infancy. The fundamentally different chemistries of hydrocarbons and of carbohydrates and lignins are perhaps pivotally important in imposing serious difficulties for their use as organic raw materials. Our fossil carbon-based economy relies on distinctly hydrophobic hydrocarbon molecules that are devoid of oxygen and functional groups. In contrast to hydrocarbons, carbohydrates are highly functionalized and hydrophilic molecules. Because environmental pressures are mounting and our dependence on fossil fuel continues to grow, any prevailing economic advantages for a petrochemical-based economy will likely fade away within the next 50 years. Our chemical and energy industry therefore needs to redevelop in a major way if it is to use lignocellulosic biomass as its feedstock. These considerations unambiguously dictate the need for

practically oriented scientific research and development covering a wide range of applications for the production of materials, chemicals, and energy from forest biomass.

The literature is abundant with research accounts aimed at offering an understanding of these complex chemical processes. To date no concerted effort has been made about bringing this knowledge together with the aim to connect the past with the future. Consequently, during the Pacifichem meeting of 2005 a symposium was held in Hawaii, focused at bringing together the global expertise from academia, government, and industry with the aim to disseminate their latest findings and to exchange their ideas for the future in the realm of materials, chemicals, and energy from forest biomass.'

The present ACS symposium sires volume attempts to offer the reader a thorough view of the information presented at this meeting and beyond. Despite the fact that the material emerged from a symposium, it is not a collection of fragmented research findings in the form of conference proceedings. Most chapter contributors have successfully attempted to provide a good review of the literature, creating a sound foundation for the science to be subsequently developed. Furthermore, a collection of authoritative reviews is also provided at the onset of the book prior to embarking on specific topics.

In an effort to convey the material in a coherent fashion the 33 chapters of this book have been divided into the following distinct sections that deal with:

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Critical Reviews
Materials from Forest Biomass
Chemicals from Forest Biomass
Energy from Forest Biomass
Novel Analytical Methods for the Structural Elucidation of Forest Biomass

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To illustrate the excellence of material that is in store for the readers of this volume, we offer now brief comments on some of the papers selected at random

Chemicals, Materials, and Energy from Biomass: A Review
Lucian A. Lucia, Dimitris S. Argyropoulos, Lambrini Adamopoulos, and Armindo R. Gaspar (all of North Carolina State University)

There are approximately 89 million metric tonnes of organic chemicals and lubricants produced annually in the United States. The majority of these are fossil fuel-based materials that have the potential to become environmental pollutants during use and that carry end-of-life cycle concerns such as disposal, pollution, and degradation. As a result, the need to decrease pollution caused by petrochemical usage is currently impelling the development of green technologies. It is virtually inarguable that the dwindling hydrocarbon economy will eventually become unsustainable. The cost of crude oil continues to increase, while agricultural products see dramatic decreases in world market prices. These trends provide sufficient basis for renewed interest in the use of biomass as a feedstock and for the development of a lignocellulosic-based economy as the logical alternative to fossil fuel resources.

Transforming Academic Curricula: From Pulp and Paper to Biobased Products
Shri Ramaswamy, Ulrike Tschirner, and Yi-ru Chen
(all of University of Minnesota)

This paper describes the ongoing efforts at the University of Minnesota to transform the academic curricula to meet changes anticipated within the forest products and pulp and paper industries. The new program places emphasis on the efficient utilization of renewable bio-resources including forestry, agricultural residue and other biomass. The department-wide transformation of teaching and learning practices has been undertaken through the reformation of degree programs, the development of curriculum and the improvement in instructional strategies. The specific objectives are organized around key thematic areas and include developing and implementing a new, transdisciplinary, inter-collegiate, bio-based products engineering and marketing and management degree program. The broader impacts of the ongoing effort include the transformation of an academic curriculum in the emerging field of bio-based products, training well-prepared technical and business professionals for the future "bio-economy."

Composite Materials from Forest Biomass: A Review of Current Practices, Science, and Technology

Renewable and sustainable composite materials can be produced using forest biomass if we maintain healthy forests. Small diameter trees and other forest biomass can be processed in the forest into small solid wood pieces, sliced veneers, strands, flakes, chips, particles and fiber that can be used to make construction composite products such as glued-laminated lumber, plywood, structural composite lumber, flakeboard, particleboard, fiberboard, and molded materials. It can also be combined with other resources to make new materials taking advantage of the unique properties of each resource. Non-construction composites can also be made such as geotextiles, filters, sorbents, packaging and nano-materials. The adhesive used in the various products depends on the intended application.

Surface and In-Depth Modification of Cellulose Fibers

This paper is divided into three parts, according to the application envisaged for the modified fibers, namely (i) as reinforcing elements in macromolecular composite materials; (ii) in wood densification and protection; and (iii) for trapping organic pollutants. The major emphasis in the first part is devoted to the controversial aspects related to the interactions between cellulose and siloxanes. The second part illustrates the approach through the use of bifunctiqnal coupling agents and the subsequent grafting of the densifying polymer. The third part shows how admicelles or aliphatic brushes, built around the fibers, playa useful role in capturing organic impurities from aqueous media.

Opportunities for Hardwood Hemicellulose in Biodegradable Polymer Blends

Hardwoods indigenous to the northeastern U.S., including birch, beech, maple and short-rotation woody crops such as willow, are relatively rich in the hemicellulose xylan. In this study, a combined biodelignification and hot water extraction procedure was employed to isolate polymeric xylan in its native acetylated state. To enhance the mechanical properties of xylan as a biodegradable material, solutions of xylan were mixed with solutions of commercially available cellulose esters followed by casting into solid films. In this fashion, it was possible to prepare acetylated xylan/cellulose triacetate "blends" with mechanical properties comparable to the cellulose triacetate itself up to 25 wt% xylan. Plasticizers were effective in increasing the strain to break for these materials but lowered the modulus at 1 % strain.

Hydrogels from Polysaccharides for Biomedical Applications

Development of products made from renewable sources is considered to be a strategic research area by the international scientific community since it is generally accepted that the fossil fuels will be exhausted in the foreseeable future. Another related strategic area is the development of new bioactive and biocompatible polymers capable of exerting a temporary therapeutic function. Among other substances, polysaccharides have been proposed to be suitable materials as matrixes for the preparation of hydrogels, e.g., for use in key applications such as drug release systems and tissue engineering. Methods reported for preparation of hydrogels using renewable polysaccharides aimed for biomedical use are reviewed in this paper.

A Brief History of Lignin-Containing Polymeric Materials Culminating in X-ray Powder Diffraction Analyses of Kraft Lignin-Based Thermoplastic Polymer Blends

The past 30-year history of lignin-containing polymeric materials has been fashioned by changing perceptions of macromolecular lignin structure. The first formulations originated in a view of lignins as "three-dimensionally branched network" polymers. Whether incorporated covalently or noncovalently into polymeric materials, lignin preparations were, with few exceptions, limited to maximum contents of 30 -- 45% (w/w). However, once the significance of noncovalent interactions between the constituent molecular components had been recognized, it was possible to generate promising polymeric materials composed exclusively of ethylated and methylated kraft lignin, and other equally simple lignin derivatives. Plasticization of these materials can be achieved in a predictable way by blending with miscible low-T_g polymers. X-ray powder diffraction analyses have helped to identify characteristic variations in the separation distances between aromatic rings that accompany such plasticization effects.

Production of Chemicals from Cellulose and Biomass-Derived Compounds: Advances in the Oxidative Functionalization of Levulinic Acid

This paper presents new data regarding the oxidation of levulinic acid (4-oxopentanoic acid), which can be considered as one of the most significant cellulose-derived compounds. The various synthetic applications of these procedures for the preparation of fine-chemicals and commodities are also discussed, with particular attention on the reactions that use homogeneous and heterogeneous rhenium catalysts. Such systems are able to activate hydrogen peroxide under mild experimental conditions causing selective oxidation chemistries.

Catalysis of the Electrooxidation of Biomass-Derived Alcohol Fuels

Oxidation of biomass-derived fuels such as methanol can serve as an energy source in applications such as the direct methanol fuel cell (DMFC). Electrocatalysis of methanol oxidation by heterobimetallic complexes provides a possible alternative to catalysis on the surface of bulk Pt/Ru anodes in DMFCs. Electrochemical oxidation of methanol has been demonstrated to .be catalyzed by a series of RuPt, RuPd and RuAu complexes.

Knots in Trees: A Rich Source of Bioactive Polyphenols

Knots in trees, i.e. the branch bases inside stems, contain extraordinary high amounts of polyphenols, which are potent natural antioxidants and biocides. Studies of more than 50 tree species have shown that knots, in most of the studied species, contain remarkably higher amounts of polyphenols than the adjacent stemwood, for many species 20-100 times higher. Knots of softwood species typically contain 5-15% (w/w) of polyphenols, with lignans as the dominating group. Pine species contain a high percentage of stilbenes in their knots, while flavonoids are abundant in knots of certain hardwood species. Spruce knots nom Northern Finland contain on average about 10% of lignans. The dominating spruce lignan 7-hydroxymatairesinol (HMR) is a strong antioxidant and has moreover been found to inhibit growth of certain tumors. Production of HMR and marketing it as dietary supplement in the USA has recently been started. In a large pulp mill using Norway spruce wood it is possible to sort out knots and extract up to 100 tons of HMR per year.

Integrating Black Liquor Gasification and Pulping: A Review of Current Technology

Gasification of black liquor could increase the flexibility and improve the profit potential of the paper industry. Its implementation would enable the application of modified pulping -technologies, while creating a synthetic product gas that could be utilized in the production of value added products or electrical power. Black liquor gasification produces output streams that can be used with great benefit in modified pulping operations. Split sulfidity and polysulfide modifications to the kraft process lead to yield increases of 1-3% points with improved product quality. Modified sulfite pulping technologies resulted in yield increases of 5-18% points with much higher brightness and significant capital and operating cost savings.

Production of Activated Carbon from Biochar Using Chemical and Physical Activation: Mechanism and Modeling

Biochar, a solid product of fast pyrolysis of biomass, was converted to activated carbon by physical (steam) and chemical (potassium hydroxide) activation. The effects of operating conditions on the BET surface area and the reaction yield of physically and chemically activated carbons were investigated. Two models for BET surface area and reaction yield of each activated carbon were developed. Using these models, the optimum operating conditions for production of activated carbons with large surface area and high yield were determined. The BET surface area and yield of products predicted by models and from experiments at optimum operating conditions showed good agreement. The effects of activating agent on the chemical structure of biochar, during chemical activation, were investigated by thermogravimetric method and infrared spectroscopy.

Measurement of Cellulase Activity with Piezoelectric Resonators

The dynamics of cellulase binding and the activity on thin films of cellulose by using a piezoelectric sensing device (Quartz Crystal Microbalance with Dissipation monitoring, QCM-D) were examined. Upon exposure of the cellulose film to enzyme mixtures, a reduction in the sensor's frequency due to molecular binding is observed. Thereafter the frequency increases due to the loss of

effective mass caused by the degradation of the film (enzymatic attack). In this study, it is demonstrated that the rate at which degradation of the film occurs can be monitored and quantified *in situ* and in *real time* as a function of enzyme concentration, temperature and pH of the incubating solution. Also, mass transport effects can be investigated by changing the flow conditions within the QCM-D reaction cell. The use of piezoelectric sensing to characterize and monitor the mechanisms and kinetics of enzyme activity on cellulosic substrates adds another dimension to our knowledge and to the methods available for such investigations.

Chemiluminometry of Cellulosic Materials

The emission of light as a result of chemical reaction during degradation of polymers has been studied since the early 1960s. Many polymers have been studied' in depth so far, and chemiluminometry has entered industrial labs as a routine investigation technique. It is particularly attractive due to the absence of sample preparation, its non-invasiveness and simplicity of instrumentation. The data can be rapidly obtained, often in the early stages of oxidation, and the technique is complementary with other approaches. However, due to the often-encountered multitude of simultaneous chemiluminescent reactions, the interpretation of data is rarely straightforward.

Contributors to the volume are affiliated with universities and research units in Portugal, France, USA, Sweden, Austria, Japan, Canada, Slovenia, China, Venezuela, Finland, and Indonesia. All their contributions are reinforced with an extensive list of references for consultation and study. Remarkable indeed.

This ACS volume will provide a resource for new ideas, guidance, and a good embarkation point for any future endeavors in materials, chemicals, and energy from forest biomass. The accounts in every paper will serve a range of readers from casual technologically oriented browsers and enthusiasts to dedicated scientific research community.

If there were more conferences of this kind at more frequent intervals and volumes of this kind were made available, there would be no more the divide that you see now between our willingness to put in efforts at exploitation and the abundant resources available and waiting to be tapped.

The papers provide a good review of the literature, creating a sound foundation for the science to be subsequently developed, making the volume absolutely outstanding. I have not seen a conference volume for the science and technology community that did such a wonderful job of presenting a resource for new ideas so clearly. I myself learned some connections I had never thought of, nor even visualized.

The collection is indeed notable for the daring leaps over knowledge gaps and future endeavors that every science and technology individual will be ready to make. If you want to understand likely and promising future endeavors in materials, chemicals, and energy from forest biomass and what it implies for the coming years, this book is an unparalleled introduction and resource and it is therefore an important part of the armamentarium of every one involved in biomass and all it implies for the future.