PULP PRODUCTION AND PROCESSING: FROM PAPERMAKING TO HIGH TECH PRODUCTS, Valentin I. Popa (Ed.), Smithers Rapra Technology Ltd, Shawbury, Shropshire, SY4NR, UK, 2013, 520 pp., ISBN 978-1-84735-634-5

The production of pulp and paper is an important economic activity based on renewable resources. By implementing the newest technological findings, this industry has lately increased its environmental friendliness and sustainability. New concepts, such as biorefining, have emerged, which, transferred into practice, aim at increasing the potential and products diversity of the pulp and paper industry, already acknowledged by some works as a "first generation biorefinery". In this context, there are multiple opportunities of developing new methods for the valorization of lignocellulosic biomass towards materials, chemicals and energy. The book reviews the progress and state of the art of the technologies and methods for conversion of cellulosic materials up to high-tech products with a wide range of applications.

The first book chapter, *Biorefining and the Pulp and Paper Industry* (Valentin I. Popa), constitutes a comprehensive description of the biomass composition and properties and possible technological approaches for its valorization. In the introductory part, the pulp mills are described as having the characteristics of biorefineries. This is justified by the fact that the modern pulp mills make use of the entire organic feedstock to produce materials (pulp fibers) and energy. Furthermore, by being energy efficient, the excess organic materials (mostly lignin) are to be extracted and processed to various chemicals and fuel types. Thus, the modern pulp mills may be easily assimilated to a biorefining facility satisfying the definition provided by most of the literature in the field. Having in mind the diversity of vegetal world, a particular attention was given to the chemical composition of available biomass, subchapter 1.2.2 being particularly dedicated to plant cell wall components. Routes of biomass fractionation and possible separated products are described as possible ways of integration in the pulp industry. Lignin is one major lignocellulosic biomass component and is worth particular attention. Separation of lignin from the black liquor is one way of using the current energy excess of pulp mills. Separated lignin is envisaged as a possible source of high energy upgraded fuels, chemicals and raw material for synthesis gas production. Polysaccharides and their degradation products, which are also contained in the black liquor, represent a source of different chemicals. In the conclusions, the plant cell wall biomass is foreseen as an important raw material for the new biorefinery plants, which should display a high level of integration and optimization for the efficient separation of components.

The second chapter, *Pulping Fundamentals and Processing* (Dan Gavrilescu), describes the main aspects of the most important route of lignocellulosic material processing. The pulping processes generate fibrous materials with various levels of lignin content, which represent the raw material both for papermaking and for the production of cellulose derivatives. The chapter includes descriptions of the main pulping processes: mechanical pulping, thermomechanical pulping, chemithermomechanical pulping and chemical pulping. A large extent of the work is dedicated to the kraft pulping reasoned by the fact that this dominates the worldwide pulp production. Organosolv pulping processes, described in the last part of this chapter, represent an environmentally friendly alternative of the kraft pulping, making use of organic solvent for lignin dissolution and fiber liberation. The development of such processes is intended to overcome some major drawbacks of kraft process, such as generation of malodorous gases and other environmental impacts, and relatively low pulp yield. Issues, such as solvent costs, recovery options and lower pulp quality obtained by using organosolv technologies, have prevented such methods from replacing conventional pulping methods at a large industrial scale.

Chapter 3 C*hemical Pulp Bleaching* (Ivo Valchev) discusses the most important issues regarding bleached pulp production. The residual lignin and other chromophores present in unbleached pulp may be removed by using different bleaching agents, therefore improving optical properties, such as brightness. Conventional elemental chlorine bleaching is omitted due to the fact that it is probably considered obsolete and polluting. Different stages of the bleaching technologies, such as oxygen delignification, chlorine dioxide, peroxide and ozone, are overviewed, along with reaction mechanism, kinetics, process parameters and technology details. The use of enzymes in the bleaching process, particularly of xylanases, is regarded as a success story of biotechnological approaches in the pulp industry.

The fourth chapter is dedicated to the probably most important development in pulp bleaching technology. *Oxygen Bleaching* (Jorge Luiz Colodette, Daniela Correia Martino) presents the fundamental aspects of oxygen alkali residual lignin pulp removal integrating the most important advantages, but also drawbacks. Starting with the basics of on site oxygen production by either the cryogenic or non-cryogenic methods, the discussion further proceeds to the elements regarding delignification chemistry and integrates technology description together with the process parameters and control issues or impact on the bleaching effluent load.

The fifth chapter, *Chemistry and Physics of Cellulose and Cellulosic Substances* (Miloslav Milichovsky), deals with interesting information on the physico-chemical properties of cellulosic materials. The work includes aspects of cellulose polymorphs and investigation methods. Furthermore, the interactions in the water-cellulose/cellulosic substances systems are described considering the existence of supermolecular and hypermolecular shapes of this compound, which is water inter-connected.

The sixth chapter *Physico-chemical Characterization of Cellulose from the Broussonetia payrifera Bark and Stem and Eucommia ulmoides Oliver Stem* (Feng Peng, Jing Bian, Pai Peng, Xue-Ming Zhang, Feng Xu and Run-Cang Sun) deals with the characterization of cellulose obtained from naturally occurring plants, such as paper mulberry and eucommia, the latter being cultivated for medicinal uses. The work focuses on analyzing the structure and thermal properties of the α-cellulose isolated from different parts of the concerning plants' tissue.

Papermaking is currently the most important and widely used method of adding value to cellulose fibers. This subject is tackled in the seventh chapter, *Cellulose Fibres in the Papermaking Process* (Florin Ciolacu), which overviews the raw materials in the paper production. The importance of recovered paper as sources of secondary fiber is emphasized, as well as the importance of the papermaking properties and suitability of cellulose fibers. The question regarding the suitability of the fibers for papermaking is thoroughly discussed taking into account important properties, such as chemical composition, morphological features and dimensional distribution, cell wall thickness and fiber coarseness and wet or dry fiber properties. The transformations of the fibers during the papermaking process are pictured taking into account different scenarios, such as integrated or non-integrated paper mills. The refining process is also considered as an important route of inducing fiber structural modification and modifying the properties of the obtained paper. The chapter ends with several conclusions on the importance of cellulose fibers as raw materials in papermaking, the need for continuous exploration of their changes during the processing pathway and also on regaining the papermaking potential of secondary fibers.

Esterification of cellulose has opened important ways of creating new and useful materials with a wide range of applications. Chapter eight, *Cellulose Esters - From Traditional Chemistry to Modern Approaches and Applications* (Diana Ciolacu, Liliana Olaru, Dana Suflet and Niculae Olaru) covers an important section in cellulose chemistry. Since 1865, the year of the discovery of cellulose acetate by Schützenberger, major discoveries and developments have been made, therefore important progress from the initial esterification methods involving acid chlorides or anhydride have to be noted. The most consistent research efforts have been made regarding the possibility of overcoming some important disadvantages of classical esterification methods, such as the long reaction times and solubility in adequate solvents. Most of the improvements on the esterification processes have been achieved by using new solvent systems, new catalysts or reaction conditions including microwave or enzyme assistance. Particular attention is given to the cellulose solvent systems taking into consideration that the dissolution of nature's most abundant polymer is an important step in the homogenous esterification process. Cellulose esters have lately been found to be of great value in the nanotechnology. Electrospinning and electrospraying have proven to be versatile methods in producing nanostructured cellulose derivatives and thus new ways of producing nano-composite materials are currently under development. These materials are to be applied in many medical and engineering fields.

The processes of production of new and improved cellulose fibers are the subject of the ninth book chapter – *Lyocell Processes and Products* (Patrick A. White and Heinrich Firgo). The processes date back to the 70's and were developed with the aim of producing improved cost/performance fiber together with an increased environmental responsibility. The beginning of these processes is identified in 1968, when Eastman Kodak developed the first methods for the dissolution and regeneration of cellulose in cyclic amine oxide. From the origin up to present, the production of regenerated cellulose fibers continuously increased following the needs of the market. The production process and different technological aspects are discussed in the chapter. Parameter controls in different stages, such as temperature of cellulose NMMO solution, are peculiarly important. The TENCEL fibers processing and conversion to yarn and fabrics are discussed at the end of the chapter, including the usage of these materials for the production of non-woven or paper type products.

By dealing with *Functional Cellulose Microspheres* (Jani Trygg, Martin Gericke and Pedro Fardim), chapter ten provides useful information on the possibility of creating and using functionalized cellulose spherical particles. These 10 µm particles may be either physically or chemically modified to satisfy different needs and desired properties according to the applications intended: liquid chromatography columns, protein immobilization, and drug delivery. The first stage in the route of preparing such particles is the dissolution of cellulose in conventional solvents or in the so-called "green solvents". The conventional solvent systems are briefly reviewed together with their advantages and disadvantages. By having the advantage of being less toxic and posing fewer threats to the environment, the green solvents are an environmentally friendly alternative. Pretreatments of the cellulose fibers facilitate the access of the chemicals to the inner structure of the fiber, but also aim at lignin and hemicelluloses removal. The techniques of microsphere preparation include dispersion at different levels of stirring, thus manipulating the dimensions of the spheres. During the coagulation stage, the properties of the microspheres may be modifed. The chapter concludes with the idea that more research is needed to fully understand the potential of these materials.

The production of micro and nanocellulose fibers opens new ways for using cellulose as new environmentally friendly replacement of some market materials. The 11^{th} chapter, *Processing Cellulose Fibers to the Micron and Nanoscale* (Youssef Habibi) reviews the most important methods of obtaining these resourceful new types of materials, which may be used for interesting applications, such as foams and aerogels, films and nanopapers or polymeric nanocomposites. Starting with a short but comprehensive presentation of the cellulose fiber ultrastructure and morphology, the discussion is further continued by the description of the methods of producing microcrystalline and nanocrystallyne cellulose. In short, both types of cellulosic preparation may be obtained by sequences of treatments involving acid hydrolysis and disintegration. Pretreatments of fibers, such as enzyme hydrolysis, alkaline steam explosion and Tempo oxidation, are intended to reduce energy consumption in the disintegration stages. The conclusions of the chapter point out to the significance of the scientific and technological challenges of the production and further applications of micro and nanocrystalline cellulose.

Cellulose esters have long been used as photographic films due to their good transparency. In the perspective of using cellulose esters for high tech applications, such as the production of liquid crystal displays, the optical properties of these derivatives have a tremendous importance. Therefore, chapter 12 *Optical Properties of Cellulose Esters and Applications to Optical Functional Films* (Masayuki Yamaguchi and Mohd Edeerozey Abd Manaf) is especially dedicated to the description of these groups of characteristics and their applications. The chapter includes the fundamentals of the optical properties of polymeric materials films and further debates particular issues regarding the cellulose derivatives, such as esters. Optical anisotropy plays an important role in establishing the optical properties of the polymer, and therefore is also taken into consideration together with the methods of controlling it, such as the modification of the substitution groups. It is concluded that developing cellulose esters with positive birefringence may be achieved by introducing propionyl and butyryl groups, while negative birefringence is induced by the acetyl groups.

The fight against disease-causing microorganisms has long been fought by using of antibiotics. The main drawback of the antibiotics usage is the evolution of certain bacteria to antibiotic resistant forms. Chapter thirteen, *Antibacterial Fibres* (Josefin Illegard, Lars Wagberg and Monica Ek) develops the idea of the current and potential usage of cellulose fibers in the manufacturing of different commercial products for prevention and fighting of bacterial caused diseases. From products such as wet wipes to advanced design sport equipment or band aids, all of the existing products and further developments are driven by the need of protection against unwanted microbial development. The chapter outlines the routes for the production of antibacterial materials and also reviews the methods of controlling the release of the active agents and the testing of the obtained products. Methods of production of antibacterial fiber based products, such as adsorption and grafting of different bioactive polymers, are included. Having the advantage of being renewable, cellulose fibers may constitute raw materials for the mass production of life-saving goods.

Recent Advances in the Processing of Biomass for Biohydrogen Production (Ioannis A Panagiotopoulos and Emmanuel G. Koukios) is the 14^{th} and the last book chapter and deals with the topical and interesting theme of biomass conversion to hydrogen production as a way to outcome different environmental aspects, such as global warming resulted from the intense use of fossil fuels. The characteristics of biomass, such as renewability and carbon sequestration, recommend them as alternative feedstocks in different chemical and energy facilities. Advanced biomass usage such as conversion to second generation ethanol or other biofuels represent a hot issue since these technologies are regarded as immature. On the other hand, the generation of hydrogen from biomass is regarded as a more facile alternative process of valorization. The pretreatments of lignocellulosics by mechanical, thermal, chemical or enzymatic means, which facilitate the access of hydrogen producing organisms to the substrate, are reviewed and considered as an essential stage in the process of biomass to hydrogen production. Sugar rich raw materials, such as sugar beet and sweet sorghum, contain readily available sugar, which may be used for hydrogen fermentation in hot climate areas. Complex organic materials, such as agricultural, food, paper or municipal wastes, have lately received attention and have been proposed as potential substrates. The fermentation stage employs bacteria, such as *Caldicellulosiruptor saccharolyticus* or *Thermotoga neapolytana*, which consume either glucose or xylose or both. One identified disadvantage of the dilute acid hydrolysis is the formation of inhibitors, such as acetic acid, furfural and derivatives or phenolic derivatives resulted from lignin degradation. To overcome this difficulty, hydrolysis conditions need to be optimized in such a manner that the generation of inhibitors should be minimal. The final remarks of the chapter outline that the pretreatment sequence is of particular importance for liberation of fermentable carbohydrates and should be carefully chosen by taking into account the category of biomass used. Future research is needed for the generation of highly fermentable substrates to maximize the bio-hydrogen production.

By gathering both interesting and important information, starting with the chemical composition of biomass, pulp production processes, papermaking and further to different types of advanced materials, the book constitutes itself as a promising knowledge resource for researchers, postgraduates, students and for any others concerned with renewable resources processing. The entire work is the result of the contributions of renowned specialists from areas concerning pulp, paper and cellulose derivatives production and is accompanied by an index to facilitate the access to different issues.

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LIGNOCELLULOSE BIOREFINERIES, Jean-Luc Wertz and Olivier Bedue, EPFL Press, 2013, 527 pp., ISBN 978-2-940222-68-1 (PFL Press); ISBN 978-1-4665-7306-2 (CRC Press)

It is known that biomass represents a renewable resource assured by the biosynthesis process. According to the definition, biomass is any organic matter that is available on a renewable basis, including dedicated energy crops and tree, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes and other materials. Due to its composition, from biomass we can obtain, by complex processing, almost all chemicals resulted from petrochemistry. That is why, considering the exhausting fossil resources, it is expected that in the future biomass will satisfy all our needs.

This comprehensive book covers practically all aspects, from the possibilities to increase the accessibility of raw materials to their conversion to different chemicals and energy sources. In chapter 1 – **Introduction** – a review is presented concerning aspects of climate change (the earth's energy budget and greenhouse effect, carbon cycle), biomass and its conversion to products, biorefineries and the life cycle assessment, which are connected with the structure of the book. In chapter 2 – **Photosynthesis, the ultimate beginning for biorefineries** – the elements involved in photosynthesis are analyzed (chloroplasts, photosynthetic pigments and antenna complexes), along with the stage of photosynthesis (light reactions and dark reactions) with examples of efficiency of the process in the case of different plants. Chapter 3 is dedicated to the **Futures of first generation biorefineries**. In this context, the possibilities to use sugar, starch and vegetable oil feedstocks are known. By using these raw materials, it was possible to obtain the first generation of biofuels (bioethanol, ethyl tert-butyl ether), biodiesel, biogas and other liquid biofuels. At the same time, some examples of biobased chemicals and materials from food plant are mentioned. To develop industrial production, the important aspects of life cycle assessment and sustainability are considered.

As mentioned above, biomass processing has to be discussed from the composition viewpoint. Therefore, in the following chapters the main structural components of biomass are presented, along with their biological and chemical stability. Thus in chapter 4 – **Cellulose, the predominant constituent of biomass** – information concerning the structure (at the molecular, supramolecular and morphological levels), biosynthesis (enzymatic polymerization of glucose in bacteria and plants), properties (mechanical and physical) and applications (in paper and man-made fibers production), is offered. Chapter 5 – **Enzymatic and non-biological degradation of cellulose** – demonstrates that the structural complexity of cellulose represents a major problem in its degradation to obtain precursors, which can be used in obtaining biofuels and chemicals. The enzymatic degradation could be applied on a large scale by improving biochemical systems to access and hydrolyze cellulose, yields in the fermentation steps and optimization of biomass pretreatment conditions. The biodegradation of cellulose can be carried out using enzymes produced by bacteria and fungi to convert the insoluble substrate to soluble sugars. Therefore, important subjects are represented by producing cellulases and understanding the mechanisms of cellulose degradation. In this chapter, detailed information is provided on the composition of the enzymatic complex for different microorganisms (fungi and bacteria), mechanism, kinetic and activity. Despite its chemical stability, cellulose can be degraded non-enzymatically by acids, oxidants, thermal energy, mechanical means and radiation. From the large amount of information existing in this field, the authors retained the main aspects concerning the mechanism and products that can be obtained following degradation, and underline the physical and chemical ways in biomass pretreatment. **Hemicelluloses and lignin, other key constituents of biomass** are presented in chapter 6. Hemicelluloses represent one of the three major components of biomass and are present under various forms in all green plants. The structure and occurrence, biosynthesis, their role in the cell wall, properties and applications are described in this chapter. Lignin is a complex phenolic polymer that imparts strength, rigidity and hydrophobicity to plant secondary cell walls. The structure and distribution of lignin are analyzed along with its biosynthesis process and the interaction with other components of the cell wall. Although lignin is extremely recalcitrant to degradation, this process is possible by the action of basidiomycetes white-rot fungi, which are able to degrade lignin efficiently using a combination of extracellular lignolytic enzymes, organic acids, mediators and accessory enzymes. This process is described in detail with a presentation of the enzymes that are involved in the degradation of lignin. At the same time, it is mentioned that lignin can represent a polymer with both low- and high-value applications, which are expected to become enormous over the upcoming decades. Many structural and compositional factors hinder the enzymatic digestibility of cellulose present in lignocellulosic biomass. That is why, pretreatments are necessary, as presented in chapter 7 – **Pretreatments of lignocellulosic biomass**. The goal of any pretreatment is to alter the structure of the lignocellulosic materials to make cellulose and hemicelluloses more accessible to the enzymes that convert polysaccharides into fermentable sugars. The pretreatment methods can be divided in the following categories: physical pretreatments of biomass involving milling and high-energy radiation, chemical methods involving liquid hot water, dilute and concentrated acids, alkali, organic solvent, oxidizing agents and ionic liquids, physico-chemical methods involving steam explosion, ammonia pretreatments, CO_2 explosion, mechanical/alkaline pretreatments and biological methods. As a conclusion, the authors summarize that biomass pretreatment remains the bottleneck in the processing of lignocellulosics for biofuels and other biobased products. Although some pretreatment methods show apparent advantages, it is unlikely that one method will become the method of choice for the diversity of biomass feedstocks, which can react differently to a given technology. Lignocellulosic biomass feedstock can be converted to biofuels and chemicals through multiple processes. Conversion technologies fall into two main categories: biochemical conversion and thermochemical conversion. **Biochemical conversion of biomass** represents the subject of chapter 8. The main steps of this process are represented by pretreatment, hydrolysis and fermentation. Pretreatment can fractionate the cellulose, hemicelluloses and lignin components. For carrying out hydrolysis and fermentation, there are different strategies including separate enzymatic hydrolysis and fermentation, simultaneous saccharification and fermentation, simultaneous sachharification and co-fermentation and consolidated bioprocessing. Along with ethanol, fermentation allows obtaining lactic and succinic acids, important precursors for other bioproducts. In this chapter, the life cycle assessments are discussed and the results obtained by different companies at different levels are presented, including not only ethanol, but also other chemicals. The chapter also offers some examples concerning lignin uses, which can significantly increase the competitiveness of cellulosic ethanol technology. The thermochemical platform for conversion of lignocellulosic biomass aims to efficiently produce biofuels and chemicals via processes that use heat and chemistry (chapter 9 – **Thermochemical conversion of lignocellulosic biomass**). Primary routes for biomass thermal conversion are the following: combustion, gasification and pyrolysis. Different variants are analyzed, along with life cycle assessments. At the same time, in this chapter case studies are presented and some information concerning the technology used, products and technology scale is systematized.

The last chapter is dedicated to **Perspectives**. It is mentioned that the biorefineries were identified as a potential solution to mitigate the threat of climate change and to meet the growing demand for energy and non-energy products. The comparison between first generation and second generation biorefineries, which generated the "food versus fuel" debate, demonstrates that the latter variant, which involves the use of lignocellulosic feedstocks, such as organic wastes and residues, and their conversion into energy and chemicals, has multiple advantages. At present, there are representative programs both in the USA and EU stimulating the improving of both feedstock yield and composition of biomass (plant genomics, breeding programs and the chemical engineering of desirable traits – drought resistance, photo-cycle intensity, cold tolerance, sugar composition C5/C6) and processes (biochemical platform and thermochemical platform). Developing these technologies can allow obtaining fuels and chemicals according to the principles of sustainability.

This book represents a valuable instrument to serve as a reference for policy makers, industry leaders, professors, teachers, scientists, engineers and students who are involved in promoting the bioeconomy.

Valentin I. Popa