Hydrothermal Processing in Biorefineries

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Editors

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Production of Bioethanol and High Added-Value Compounds of Second and Third Generation Biomass

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Preface and Editorial

Biomass from lignocellulosic and aquatic material is seen as an interesting source of raw material for conversion into biofuels, biochemicals, and biomaterials that are coproduced via biomass upgrading. The main reason is that biofuels such as bioethanol and new bio/co-products with high added value can contribute to sustainable development. Subsequently, both are attractive in industry and the bioeconomy in terms of an integrated biorefinery for second and third generation.

The integrated biorefinery concept is centered on environmental and economic aspects. Therefore, the pretreatment process plays an important role in an integrated biorefinery, since this stage allows the fractionation of the main components of the lignocellulosic and aquatic biomass. Hydrothermal processing is easy to operate and is the first step allowing the solubilization and depolymerization of the hemicellulose fraction while increasing the accessibility of cellulose to enzymes producing sugars for bioethanol production. Thus, hydrothermal processing is a potential technology to convert raw materials such as lignocellulosic and aquatic biomass into bioenergy and high added value compounds. In the near future, second- and third-generation biofuel facilities are expected to develop toward the biorefinery concept. The biorefinery economy is a vision for a future in which renewable energy from biomass replaces fossil fuels.

This book aims to show fundamental concepts and key technological developments that enabled industrial application of hydrothermal processing on lignocellulosic and aquatic biomass in terms of biorefineries. This book brings together experts in the application of hydrothermal processes on lignocellulosic and aquatic biomass.

This book is dedicated to Prof. Esteban Chornet and Dr. Ralph P. Overend in recognition of the role that they have played in the development and application of severity parameter as a variable to measure the hydrothermal processing, and also we want to dedicate to the Memory of Professor Ortwin Bobleter (Institute of Radiochemistry, University of Innsbruck, Austria), who passed away in September 2014; he was one of pioneers of the hydrothermolysis process.

In addition, the editors want to dedicate this book to those who have established the process for using hydrothermal processing with water or steam (also called autohydrolysis, hydrothermal pretreatment, hot compressed water, hydrothermolysis, liquid hot water, aquasolve process, aqueous pretreatment pressure cooking in water, and hot water flow-through pretreatment) and severity parameter: William H. Mason† (pioneer in steam explosion process), Prof. Morris Wayman† (University of Toronto, Canada), Dr. Jairo H. Lora (Lora Consulting LLC), Prof. Robert F. H. Dekker (Biorefining Research Institute, Lakehead University, Canada), Prof. Charles (Charlie) E. Wyman (University of California, USA), Prof. Jack (John) Saddler (University of British Columbia, Canada), Prof. Lee R. Lynd (Dartmouth College, USA), Prof. Michael R. Ladisch (Purdue University, USA), Prof. Juan C. Parajó (University of Vigo, Spain), and Guido Zacchi (Professor emeritus, Lund University, Sweden), Dr. Helena Chum (National Renewable Energy Laboratory (NREL), USA), Prof. Nicolas Abatzoglou (Université de Sherbrooke, Canada) and Prof. Khaled Belkacemi (Université Laval, Canada).

We are, therefore, pleased to introduce this book on Hydrothermal Processing in Biorefineries. This book contains 21 chapters about various aspects of the use of hydrothermal processing including liquid hot water, steam explosion, raw materials, and severity parameter application.

In Chap. 1, Dr. Chornet and Dr. Overend provide a retrospective on the development of the severity factor as well as a perspective on the importance of biorefining.

In Chap. 2, the effects of hydrothermal pretreatment on lignin are reviewed. This review includes a discussion of how pretreatment conditions affect the extent of lignin removal as well as the types of products that are produced. A brief introduction to analytical techniques for lignin is also provided. As the phenols produced by pretreatment are potential antioxidants, the authors review the categorization of antioxidants, the mechanisms of antioxidant behavior, and methodologies for measuring antioxidant capacity and report the antioxidant behavior of extracts produced by hydrothermal pretreatment of biomass.

Chapter 3 examines the effects of hydrothermal pretreatment on hemicellulose. The chapter begins with a brief description of hemicellulose reactions during hydrothermal pretreatment. This is followed by a discussion of hemicellulose structure by type of biomass. Liquid hot water pretreatment and steam explosion are discussed. The reaction mechanism of hemicellulose hydrolysis is presented and relevant kinetic models are summarized. This is followed by a discussion of analytical techniques for measuring concentration and molecular size of hemicellulose-derived oligomers and monomers. Techniques for examining the structure of hemicellulose in biomass solids are also presented.

Chapter 4 presents the effects of hydrothermal pretreatment by biomass type: wood, bamboo, agricultural residues, and agave bagasse. The structure and composition of each biomass type is summarized. The chapter reviews acidic and alkali hydrothermal pretreatment conditions by summarizing the changes in hemicellulose, cellulose, lignin, ash, extractives, and ultrastructure. The effect of temperature, time, particle size, and reactor type on the outcomes of hydrothermal pretreatment is also presented.

Chapter 5 provides a review of hemicellulose hydrolysis operating conditions and reactor design. The chapter summarizes kinetic models of hemicellulose hydrolysis. Finally, the chapter describes a wide range of applications for hemicellulose derivatives including pulp additives, films, nutraceuticals, and furfural and organic acid production.

Chapter 6 describes the development of the severity parameter in greater detail. The chapter begins with an introduction on dilute acid hydrolysis and a derivation of kinetic rate expressions for hemicellulose hydrolysis. Against this background, the derivation of the severity factor and the combined severity factor is presented. Xylose yields from pretreatment, glucose yields from enzymatic hydrolysis, and total glucose plus xylose yields from a range of biomass are presented as a function of severity factor in order to identify overarching trends. Finally, the use of the combined severity factor for dilute acid hydrolysis of xylo-oligomers is examined.

Chapter 7 begins with an introduction to the effects of pretreatment on biomass as well as the need for pretreatment as a step in the production of lignocellulosic ethanol. The authors then review the families of enzymes utilized during enzymatic hydrolysis. Steam explosion, liquid hot water pretreatments, and the severity factor are discussed, particularly in relation to subsequent enzymatic hydrolysis. Building on this foundation, the authors present methods to reduce enzyme loading. This is followed by a review of inhibitor production during pretreatment and methods to reduce inhibition. Finally, the use of pretreated biomass for on-site production of enzymes is presented.

Chapter 8 examines the current state of process modeling and economic assessment of hydrothermal pretreatment and identifies opportunities for advancement and improvement. The chapter begins with a description of the pretreatment process as well as a description of auxiliary operations such as size reduction and solid–liquid separations. The chapter reviews available process simulation software and methods of modeling pretreatment reactions within the software. Techniques for calculating capital and operating costs and evaluating plant economics are also presented.

Chapter 9 summarizes the effects of pretreatment on herbaceous energy crops such as prairie cordgrass and switchgrass, the agricultural residue date palm tree fronds, and halophytic species, *Salicornia bigelovii*. The chapter also examines the performance of the same pretreated materials during enzymatic hydrolysis and fermentation.

Chapter 10 begins with a review of hemicellulose hydrolysis conditions, reactor configurations, and reaction modeling through the perspective of oligomer production. The chapter then summarizes techniques for recovering high-purity xylo-oligomers from biomass hydrolysates, emphasizing the need for multistage processing. Chromatographic and spectroscopic techniques for analyzing oligosaccharides are presented. The chapter concludes with a description of oligomer applications in functional foods, hydrogels, and films.

Chapter 11 provides a brief introduction to the structure of hemicellulose, its processing, and potential applications for the production of enzymes, xylitol, and furans. The chapter discusses in detail the activities of hemicellulases. This is followed by a review of industrial applications and world market for hemicellulases as well as the production of hemicellulases using hydrolysates produced by hydrothermal pretreatment. The applications for and production of xylitol and furans are presented. For each end product, the authors present current and emerging production processes.

In Chap. 12, Hongzhang Chen and Wenjie Sui describe the basic principles of steam explosion and integration of this process in biorefinery systems.

In Chap. 13, Nicolas Jacquet and Aurore Richel describe the adaptation of the severity factor model to fit the complex dynamics and varying operating conditions in steam explosion processes.

In Chap. 14, Ana Rita C. Morais and Rafal M. Lukasik provide the state of the art of hydrothermal processing using supercritical CO_2 as catalyst and its implementation in biorefineries.

In Chap. 15, Viviane Marcos Nascimento, Carlos Eduardo Vaz Rossell, and George Jackson de Moraes Rocha compare hydrothermal pretreatment of sugarcane bagasse in laboratory and pilot for second-generation ethanol production.

In Chap. 16, Alfred Rossner and Carolina Parra present pilot plant experiences with hydrothermal pretreatment of hardwood (eucalyptus wood) to obtain ethanol, as part of a Chilean consortium for utilization of woody biomasses called BioEnercel.

In Chap. 17 Michael Persson, Borbála Erdei, Mats Galbe, and Ola Wallberg describe techno-economic evaluation as a tool in developing more economically and environmentally sustainable second-generation biorefineries.

In Chap. 18, Adriaan van Heiningen, Yusuke Yasukawa, Kefyalew Dido, and Raymond Francis describe the use of formic acid in hot water hydrolysis as a means of minimizing precipitated lignin formation while maximizing monomeric sugar yield.

In Chap. 19, Shuntaro Tsubaki, Ayumu Onda, Tadaharu Ueda, Masanori Hiraoka, Satoshi Fujii, and Yuji Wada describe the fundamentals of hydrothermal microwave-assisted biomass processing and demonstrate this pretreatment method on seaweed biomass.

In Chap. 20, Daniela E. Cervantes-Cisneros, Dulce Arguello-Esparza, Alejandra Caebello-Galindo, Brian Picazo, Cristóbal N. Aguilar, Hector A. Ruiz, and Rosa M. Rodriguez-Jasso describe and discuss the most relevant hydrothermal processes for extraction and fractionation of seaweed molecules while keeping the properties of the active components intact.

In Chap. 21, Cristina González-Fernández, Lara Méndez, Mercedes Ballesteros, and Elia Tomás-Pejó describe hydrothermal processing of microalgae biomass as a means to disrupt the microalgae cells and hydrolyze biomass components prior to biofuels production.

The editors would like to thank all of the authors for their compelling contributions to this book and the reviewers for their willingness to assess the submitted chapters.

The text should be of interest to students, academics scientists, engineers from industry, and potential investors in the biorefinery field. We hope you will enjoy reading the chapters presented in the book as much as we enjoyed writing and editing it.

Saltillo, Coahuila, Mexico — Héctor A. Ruiz
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About This Book

The concept of a biorefinery that integrates processes and technologies for biomass conversion demands efficient utilization of all components. Hydrothermal processing is a potential clean technology to convert raw materials such as lignocellulosic materials and aquatic biomass into bioenergy and high added-value compounds. This book aims to show scientific and technological concepts that lead to developments in the industry of biorefineries applying this technology: hydrothermal processing. Also, the scope of this book is primarily for scientists working in this area of biorefineries, engineers from the industry, and potential investors in biofuels. Therefore, the information in this book will provide an overview of this technology applied to lignocellulosic materials and aquatic biomass and especially new knowledge. It is very important to note that this book brings together experts in the application of hydrothermal processes on lignocellulosic and aquatic biomass.

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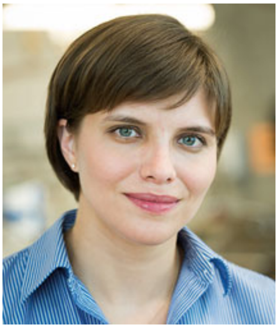
Héctor A. Ruiz obtained his Ph.D. in chemical and biological engineering from the Centre of Biological Engineering at the University of Minho, Portugal, in 2011. Then, 1 year later, he worked as postdoctoral researcher at the University of Minho (Portugal) and University of Vigo (Spain) under the supervision of Prof. José A. Teixeira and Prof. Juan C. Parajó (2012). He is currently full professor in the School of Chemistry at the Autonomous University of Coahuila and founder of the biorefinery group in the Food Research Department, Saltillo, Coahuila, Mexico, and leader of the pretreatment step in the Cluster of Bioalcohols in the Mexican Centre for Innovation in Bioenergy (Cemie-Bio), Mexico. Dr. Ruiz is currently the leader of the biorefinery group that is actively working on the development of biorefinery strategies for the production of high added-value compounds and bioethanol from lignocellulosic and macroalgal biomass. His research has been specifically on hydrothermal processing (autohydrolysis) and biorefinery strategies for the production of high added-value compounds and bioethanol from lignocellulosic, micro-macroalgal biomass. Dr. Ruiz has conducted several research stays and technical visits: at the Federal University of Sergipe (Brazil); Brazilian Bioethanol Science and Technology Laboratory (CTBE, Brazil); Chemical and Biological Engineering Department at the University of British Columbia (Canada); CIEMAT, Renewable Energy Division, Biofuels Unit (Spain); University of Jaén (Spain); Sardar Swaran Singh National Institute of Bio-Energy (India); and Tokyo Institute of Technology (Japan).

He has authored or co-authored several research publications with an *H* factor of 14 (Google Scholar Citations). Currently, Dr. Ruiz is editor in chief of the *Bioethanol* journal (De Gruyter Open, since 2014) and associate editor of the *BioEnergy Research* journal (Springer, since 2015) and participates in the editorial advisory board of *Industrial Crops and Products* (Elsevier, since 2013) and the *Biofuel Research Journal*. Dr. Ruiz was awarded with the prize "Dr. Carlos Casas Campillo" of the Mexican Society of Biotechnology and Bioengineering in 2016. This award aims to encourage young researchers and give recognition to their contributions to the development of biotechnology and bioengineering in Mexico.

Dr. Mette Hedegaard Thomsen is a Assistant Professor in the Department of Energy Technology at the Aalborg University in Esbjerg, Denmark, she has worked on the utilization of waste products and aquatic biomass for biofuels and green chemicals for more than 10 years. MHT has worked closely with European, American, and Middle Eastern industries to develop and scale up biorefinery processes and has PI experience from several national and international research projects. MHT is author and co-author of more than 60 scientific papers including 38 ISI journal papers, five book chapters, and several conference contributions in areas related mainly to bioenergy and biochemical production. Major contributions in the field of biorefineries include application of amylolytic lactic acid bacteria in the production of biopolymers, being part of the team that developed the acidification process for grass juice as substrate to produce l-lysine, being part of the team that developed the demonstration-scale hydrothermal treatment of wheat straw, chemical characterization and development of conversion processes for many different biomasses, progress in biomass-to-ethanol fermentation technology, and isolation and application of natural antibiotics.



Heather L. Trajano is an assistant professor in the Department of Chemical and Biological Engineering at the University of British Columbia in Vancouver, Canada. She obtained her Ph.D. in chemical engineering at the University of California Riverside. Dr. Trajano's focus is on exploring and harnessing fundamental knowledge of biomass fractionation and conversion for maximum economic and environmental benefit. Specific research interests include (1) fundamentals of biomass deconstruction to separate carbohydrates from lignin, (2) recovery and purification of extractives, and (3) heterogeneous catalysis for chemical production. Dr. Trajano searches for biorefining opportunities that complement existing forestry operations by utilizing waste streams and by-products.

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