

# Preface

Supercritical water (SCW) is water above its critical point (CP; 374 °C and 22.1 MPa). SCW or near critical water (NCW) is a unique green solvent with reduced polarity and a lower dielectric constant ( $\epsilon$ ) value, which provides it high solubility for many weakly-polar organics and light inorganic gases such as hydrogen and oxygen. NCW or SCW exhibits very high reactivity for conversion of biomass materials due to its greatly increased value of ion product ( $[\text{H}^+][\text{OH}^-]$ ), which could efficiently hydrolyze biomass, and hence promote many biomass conversion processes such as hydrolysis, liquefaction, carbonization, oxidation and gasification. Thus, NCW and SCW have great promise for biorefineries and conversion of biomass to produce biofuels and bio-based chemicals.

Although there are many books on the topic of either biomass conversion or SCW, the unique feature of this book is that it links biomass conversion with SCW/NCW and reactor design. This book is the second book of the series entitled *Biofuels and Biorefineries*.

This book consists of 17 chapters contributed by leading world-experts on biomass conversion with SCW/NCW. Each chapter was subjected to peer-review and carefully revised by the authors and editors so that the quality of the material could be improved. The chapters are arranged in three parts:

Part I: Fundamentals of Supercritical Water (Chaps. 1, 2, 3, and 4)

Part II: Reactor Design (Chaps. 5, 6, 7, and 8)

Part III: Near-critical and Supercritical Water Applications (Chaps. 9, 10, 11, 12, 13, 14, 15, 16, and 17)

**Chapter 1** introduces the fundamentals of hydrogen bonding in SCW and its relation to ion product and thermodynamic data of SCW for biorefining. **Chapter 2** develops a local mapping concept to describe thermodynamically consistently the saturation curve of water and biomass components, and gives results of calculations of phase equilibria and critical curves for some main biomass components in SCW. **Chapter 3** mainly provides basic characteristics of co-solvents in sub- and supercritical water and analyzes the effect of co-solvents on reactions to provide

readers with comprehensive information of co-solvents interactions. **Chapter 4** uses thermodynamic equilibrium modeling of SCW gasification (SCWG), and shows how to build a process model based on Gibbs energy minimization. **Chapter 5** introduces unique flow-through optical reactors designed to allow microscopic observations of chemical processes of biomass in sub- and supercritical water. **Chapter 6** describes a fused silica capillary reactor, which allows in situ optical observations of the sample in NCW using a microscope and spectroscopic tools (e.g., Raman spectroscopy) for kinetic studies. **Chapter 7** focuses on the use of different types of reactors for SCW oxidation (SCWO) processes. **Chapter 8** aims to discuss the effects of the reactor wall properties, operating parameters on SCWG of real wet biomasses and the associated operating challenges. **Chapter 9** discusses sub- and supercritical water treatment of biomass feedstocks for hydrochars, and presents systematic characterization of fuel properties of the resultant chars. **Chapter 10** discusses the effects of operational parameters and operational problems such as corrosion, salt deposition and carbonization in the treatment of organic wastes with SCWO processes. **Chapter 11** provides an overview on the yield of syngas and hydrogen from SCWG of biomass, and discusses the influence of different types of biomass, key process conditions as well as homogeneous and heterogeneous catalysts on gasification. **Chapter 12** introduces methane gas production via SCWG of biomass, and focuses on the effects of operating conditions and types of catalysts on the gasification efficiency and methane yield. **Chapter 13** presents a comprehensive review on catalysis for SCWG, and summarizes the development status and role of different homogeneous and heterogeneous catalysts. **Chapter 14** deals with hydrothermal bio-crude production, chemical reaction pathways and upgrading pathways of bio-crude components while focusing on hydrodeoxygenation reactions. **Chapter 15** demonstrates the generation of energy from bio-fuels using SCWO processes, and analyzes energy recovery studies of SCWO processes. **Chapter 16** reviews the production of chemicals in terms of feedstocks (biomass, plastics, inorganics and wastewaters) and reactions (gasification, oxidation, depolymerization, precipitation and hydrothermal synthesis). **Chapter 17** presents techno-economic analyses of SCWG processes for producing hydrogen from glucose and sewage sludge.

This book covers a wide range of scientific and technical aspects of SCW/NCW and the reactor design techniques necessary for efficient conversion of biomass resources to bioenergy, bio-fuels and bio-based chemicals. The text is of interest to students, researchers, academicians and industrialists in the areas of hydrothermal processing of biomass, thermo-chemical conversion of biomass, and bioenergy and bioproduct development.

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