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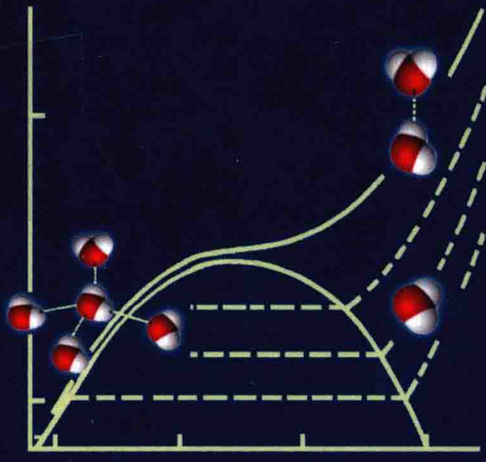
HYDROTHERMAL AND SUPERCRITICAL WATER PROCESSES

GERD BRUNNER



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Volume 5

Hydrothermal and Supercritical Water Processes

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Foreword

It is a pleasure to introduce the 5th volume in the Elsevier Book Series on Supercritical Fluid Science and Technology. This book on "Supercritical Water and Hydrothermal Processes" has been authored by Professor Gerd Brunner at the Hamburg University of Technology in Germany. Professor Brunner is one of the best known names in the field of supercritical fluids and their applications. He has vast experience and has been a leader in the field. Professor Brunner has also been a member of the Editorial Board of the Journal of Supercritical since 1988, and has been serving as the Regional Editor of the Journal for Europe since 2000.

Starting with the basics, the author presents comprehensive treatments of the application areas of importance. Chapter 1 provides a broad introduction to the essential features of supercritical water and highlights the various topics covered in the book. Just reading Chapter 1 alone, I am sure you will immediately appreciate the value of this book and share my view that this is an indispensable reference volume to all, in academia and industry, who are working with supercritical fluids or hydrothermal processes.

Chapter 2 is devoted to the thermodynamic, transport and electrical properties of water. Extensive data are presented on the volumetric properties, viscosity, thermal conductivity, diffusion, electrical conductivity, dielectric constant, refractive index and surface tension covering a wide range of temperatures and pressures. Numerous models and correlations are reviewed and discussed. Discussions on these properties and their variation with pressure are extended to mixtures of water in Chapter 3. Binary mixtures such as water + carbon dioxide and water + hydrocarbon, or ternary mixtures such as water + hydrocarbon + carbon dioxide or hydrogen are covered at length, and their phase behavior is discussed in terms of the Van Konynenburg and Scott classifications. Water–salt mixtures are also discussed.

Chapter 4 is devoted to thermal properties and heat transfer in water, which is discussed in different phase domains of water, including the gas, liquid, two-phase domain and the near critical region. Extensive documentation of the applicable models and heat transfer correlations are presented. Heat transfer in mixtures of water is also discussed with an emphasis on the greater importance of linking heat transfer with phase behavior as phase splitting is often encountered in systems involving mixtures.

Chapter 5 is devoted to water as a reaction medium. The chapter highlights the pressure-tunable nature of the properties of water and its use as variable reaction medium. A range of different reactions are covered with the majority of the discussion being devoted to hydrolysis reactions.

Chapter 6 provides a review of principles of extraction and mass transfer. The effect of factors such as pressure, temperature, solvent-solute ratio, solvent density, and particle size on extraction is discussed. Examples that involve extraction with hydrothermal or supercritical water are then presented. Among the specific applications discussed in detail are the extraction of organic compounds and heavy metals from soil, extraction of fats and proteins from bone material, and extraction of natural plant materials. Chapter 7 is devoted to reactive extractions with a focus on the extraction and liquefaction, or the gasification of coal, oil shale, and other fuel-related materials.

Chapter 8 is devoted to biomass conversions in supercritical or high-temperature water. The treatment is systematic, starting with detailed discussions of conversions of the monomeric constituent sugars (such as glucose, fructose and xylose) and the polymeric components that include starch, pectin, cellulose, hemicelluloses, and lignin. The chapter then covers in detail the conversion of lignocellulosic materials with a focus on biomass liquefaction and biomass gasification.

Chapter 9 presents depolymerization, or fragmentation of polymeric materials using high-temperature or supercritical water as the reaction medium. Among the specific applications discussed are the hydrolytic depolymerization of poly(ethylene terephthalate), nylon 6, polycarbonate, and poly(lactic acid); and the fragmentation of thermoplastics such as polyethylene and polystyrene, and of polymers encountered in fiber-reinforced plastic materials.

Chapter 10 provides a detailed treatment of oxidation reactions. Discussions are focused on hydrothermal flames and supercritical water oxidation for conversion or destruction of organic chemicals.

Chapter 11 describes the hydrothermal processing of inorganic materials for generation of fine particles, or for synthesis of metal oxides, or for control of crystal structure or morphology. Among the various metal oxides discussed is the formation of silica particles via crystallization from their water solutions.

Chapter 12 is devoted to corrosion phenomena that are of significance for process equipment in processes such as supercritical water oxidation or supercritical water based cooling systems for nuclear reactors. Corrosion principles are reviewed and corrosion behavior of stainless steel and various alloys is discussed. Protective approaches such as the use of transpiring wall reactors in supercritical water oxidation are also discussed.

The final chapter of the book describes various high-pressure laboratory systems for conducting experiments related to phase equilibria, reactions and extractions, and for equipment components that are involved in processes that involve hydrothermal or supercritical water.

This book is an authoritative account of all aspects of supercritical water and hydrothermal processes. It is rich with an extensive compilation of property data, correlations and examples of applications. I trust you will find this book to be a resource of high value in your research and teaching.

Erdogan Kiran
Series Editor
Blacksburg, VA
January 2014

Preface

This book, *Hydrothermal and Supercritical Water Processes*, presents an overview on the properties and the applications of water at elevated temperatures and pressures. It combines fundamentals with production process aspects.

Water is an extraordinary substance. It is necessary for life and is present everywhere. Water forms phenomena such as glaciers, the polar ice caps, rain, snow, fog, and contributes substantially to the greenhouse effect. Liquid water is available in underground reservoirs, in rivers, lakes, and most abundantly in the sea. Water is applied in numerous everyday activities and industrial processes.

At elevated temperatures (and pressures) the properties of water change dramatically due to the modifications of the molecular structure of bulk water that varies from a stable three-dimensional network, formed by hydrogen bonds at low and moderate temperatures, to an assembly of separated polar water molecules at high and supercritical temperatures. With varying pressure and temperature, water is transformed from a solvent for ionic species to a solvent for polar and non-polar substances.

This variability and an enhanced reactivity of water have led to many practical applications and to even more research activities, related to such areas as energy transfer, extraction of functional molecules, unique chemical reactions, biomass conversion and fuel materials processing, destruction of dangerous compounds and recycling of useful ones, the growth of monolithic crystals, and the preparation of metallic nanoparticles.

The result of the intensive research is an enormous number of scientific publications and practical applications at various stages. Most of the specialized areas of the application of water and the underlying fundamentals are covered in separate comprehensive reviews and handbooks. The original scientific papers and the compilations are both available in the literature. This book is intended as an introduction to the wide range of activities that are possible in aqueous mixtures. It is organized to allow understanding of the main features, outlines the main applications and provides access to further information. It is the intention to make enough data available that the book can be used as reference. Access to process applications is facilitated by pointing out the fundamental principle of engineering common to the very different special applications. The combination of fundamentals and detailed processing examples should lead to the awareness that these fundamentals basically determine all applications, whatever the nonconventional conditions of state or the detailed problems.

Hydrothermal and Supercritical Water Processes is a volume in a series published by Elsevier on "Supercritical Fluid Science and Technology". Therefore, there will be some overlap with other titles in this series. This book covers the most important areas of water at elevated temperatures from the point of view of the author. The different topics are presented as an overview based on the fundamentals. It is not a review and therefore does not cover all the literature, although the author has taken care to include all of the important aspects.

The book is written for undergraduate and graduate students of various disciplines, such as general chemistry, physical chemistry, geochemistry, applied physics, chemical engineering and related engineering disciplines, as well as for scientists and engineers interested in the topics presented here and being active in the field, and for all interested readers.

The production of this book needed support from many persons. I acknowledge all the help that I got in the last three years. First, I want to thank my wife Annemarie for her patience and encouragement. Then, I am very grateful to Prof. Erdogan Kiran, Virginia Tech, USA. As an editor of the book series, he asked me to write this book and followed its development with great enthusiasm and many useful comments. My thanks also go to the team at Elsevier: Derek Coleman, Susan Dennis, and Mohanapriyan Rajendran. They were very helpful and eventually produced this book from the accumulated pages. Last, but by far not least, I thank all my co-workers, who have contributed with their work. They laid the foundations for me to be able to write this book with their many PhD Dissertations, Master, Bachelor, and Diploma Theses. These are represented in the reference lists of the various chapters. The Institute of Thermal Separation Processes, directed by Prof. Irina Smirnova, of the Hamburg University of Technology provided valuable background support. I would also like to mention Ms. S. Meyer-Storckmann, who has been very helpful with providing literature.

It is my hope that this book will prove useful in extending the knowledge on and the application of hydrothermal and supercritical water.

Gerd Brunner
Hamburg
January 2014

Chapter 1

Introduction

Water is the most abundant and ubiquitous compound on planet Earth. By far, most of the amount of water occurs in the liquid state at temperatures of $T=0$–40 °C. The properties of water at these conditions are familiar. Nevertheless, a small part of water occurs at temperatures around $T=100$ °C or higher, for example, in geysers. Around such hot-water sources, minerals precipitate. Furthermore, gem-like monocrystals, like rock-crystals, are most probably the product of hot-water processes. The steam engine, pioneer of industrialization, uses evaporation and condensation of water at high temperatures. Beyond these examples, high-temperature water is useful for many other applications. These applications are the main topic of this book, which is about the fundamentals and processes of hydrothermal water, at temperatures higher than $T=100$ °C, and water in the supercritical state, at temperatures $T>374$ °C and pressures $P>22$ MPa.

The properties of water vary from ambient conditions to critical conditions and above critical conditions over a remarkably wide range. From ambient to supercritical temperature, water changes its character from a solvent for ionic species to a solvent for nonionic species. Electrochemical properties vary substantially. For example, the dipole moment decreases from its high value at ambient conditions to a value common for normal solvents at supercritical conditions. But even in the critical region, water is still as polar as acetone. The pH value of liquid water decreases by three units with temperature increasing to about $T=250$ °C, thus providing many more H_3^+ ions for acid-catalyzed reactions. Just below the critical temperature, the ionic product of water changes tremendously, rendering near-critical and supercritical water a much less ionized compound than at ambient conditions. Reactivity of water increases in the neighborhood of the critical point with or without a catalyst. These, and other properties of hydrothermal and supercritical water, are presented in Chapter 2.

Most of the applications of water at high temperatures use the interaction of water with other compounds, as in chemical reactions, extraction processes, hydrothermal processes, and others. Properties of mixtures of water with other compounds must be known for these processes. Water at ambient conditions readily dissolves salts and is not miscible with nonpolar components such as hydrocarbons. At supercritical conditions, the solvent power of water for ionic

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species is dramatically reduced. On the other hand, supercritical water and hydrocarbons become completely miscible. This behavior of aqueous mixtures is discussed in Chapter 3 for major groups of compounds, such as gases, hydrocarbons, volatile and nonvolatile electrolytes, and metal oxides.

Experimental results are shown in Chapter 3 for phase equilibria with water. A systematic classification of equilibrium behavior is presented. Modeling of phase behavior and solubility is of great importance for processes. Even for aqueous mixtures, relatively simple equations of state are able to describe the phase behavior of aqueous systems for a wide range of conditions. Solubility of gases in water can be treated in many cases with Henry's law and some modifications. Electrolytes introduce the chemical reaction of ions into the description of phase behavior. For example, carbon dioxide is a weak electrolyte in aqueous solution, but can be of influence on reactions that depend on pH value. In addition to aqueous mixtures of inert gases and hydrocarbons with water, phase behavior and solubility of volatile electrolytes, nonvolatile electrolytes, metal oxides, and salts are treated in Chapter 3. Solubility of metal oxides in hydrothermal and supercritical water is the basis for hydrothermal processes leading to monocrystals and functional nanoparticles, treated in Chapter 11.

Water has a high heat capacity and an exceptional high enthalpy of evaporation. These properties are ideal for heat transport processes. Therefore, hydrothermal and supercritical water is vastly applied as a heat-transporting and heat-transferring medium, mostly in power plants, as discussed in Chapter 4.

In many processes involving water at hydrothermal and supercritical conditions, water is by far the main component. Due to the high-temperature level, recovery of energy from the process effluents is required for economic reasons. In most cases, heat transfer to or from pure water can be taken as a first approximation. Nevertheless, in many cases, mixtures of process compounds with water are processed and split into several phases during heat recovery, thus connecting phase behavior to heat transfer processes. Condensation of mixtures from high-temperature conversion processes shows that from the incoming gaseous mixture with decreasing temperature and pressure, a gaseous phase, a hydrocarbon rich liquid phase, and an aqueous liquid phase are formed. Such cases are shown in Chapter 4.

Chemical reactions in hydrothermal and supercritical water are carried out in a wide range of conditions. Properties of the reaction medium "water" can be adjusted without adding or removing compounds from the reaction mixture. Depending on conditions of state, water thus exerts totally different actions to other compounds. For reactions at hydrothermal conditions, pressure must be higher than the vapor pressure of water to keep the reaction in the liquid phase because gaseous water loses one of the most important properties for a reaction medium: solvent power.

Several properties of water change with increasing temperature. The ionic product increases up to a temperature of about $T = 250$ °C by three orders of magnitude, the dielectric constant drops from about 80 Debye to about 2 Debye, and density decreases. But up to relatively high temperatures, liquid water maintains essentially the familiar properties of a highly polar solvent. The dramatic change occurs in the neighborhood of the critical point, the so-called critical region. Within about $\Delta T = 20$ K, properties of water change in such a way that familiar properties of water are lost. For example, water loses its solvent power for ionic species and becomes a good solvent for nonpolar components.

In the critical region, water has a density that is easily changed by pressure and temperature. While supercritical water largely loses its solvent power at low pressures, it remains a polar solvent. At higher pressures, a good solvent power and higher polarity can be reached for supercritical water. Thus, the near-critical and supercritical region is a working field for realizing different reaction conditions and for recovering products by changing conditions. Furthermore, water at near-critical and supercritical conditions is fully miscible with many organic and inorganic compounds, enabling reactions in a homogeneous medium. Therefore, supercritical water can be a reaction medium for reactions usually carried out in organic solvents.

Supercritical water is an excellent reaction medium for reactions requiring heterogeneous catalysts, since high diffusivity avoids mass-transfer limitation and high solvent power prevents coke formation and poisoning of the catalyst. The reaction rates of small free radicals are increased due to the high collision frequency. Reactions of high-molecular-mass free radicals, as they occur during pyrolysis, are slowed down by a cage effect caused by solvent molecules at high pressure. Reactions with many different compounds are described in Chapter 5.

Valuable compounds often occur in nature in materials that contain water, such as fresh plants. Extraction with hot water has been carried out for many centuries at ambient pressure. Liquid water at temperatures $T > 100$ °C and pressures $P > 0.1$ MPa extends these applications and makes available compounds that have not been accessible at low-pressure conditions. At near-critical and supercritical conditions, the effective extraction of contaminants from waste materials becomes feasible. The extraction process, characterized by solubility, kinetics, and mass transfer is treated in Chapter 6.

At lower temperatures, ionic and polar species will be extracted by water, thus creating an alternative to weak-polar supercritical solvents like CO_2. At higher temperatures, in particular, approaching the critical temperature, also nonpolar substances will be readily dissolved and extracted. In many cases, this is a physical process, where compounds are dissolved in a solvent, recovered with the solvent, and then separated from the solvent as product. But there are also many cases in which the solvent not only physically interacts with the substrate and the extract compounds but also reacts by breaking chemical bonds between substrate and extract compounds or by reacting with the compounds itself. In particular, with hydrothermal and supercritical water as a solvent, such reactions occur at elevated temperatures due to the properties and the increased reactivity of water. Useful products of this process can be the extract components, the residual substrate, or both. Examples treated in Chapter 6 are the cleaning of soil from unwanted compounds, the cleaning of bone materials, and the extraction of substances from plant materials.

Fuel materials as coal, oil shale, tar sands, and heavy bitumen can be processed with high-temperature water, as discussed in Chapter 7. Processing of fuel materials with water makes use of the advantageous properties of water, such as availability, environmental compatibility, solubility behavior, at ambient and high-temperature conditions. At low temperatures, hydrocarbons are nearly immiscible with water, while at high temperatures, the solubility increases until total miscibility occurs around the critical temperature. In parallel, the reactivity of hydrocarbons with water increases with temperature and hydrolytic and pyrolytic transformations are observed. Only simple hydrocarbons are relatively stable at near-critical and supercritical water conditions. With increasing temperature, other properties of hydrocarbons also change: viscosity is drastically reduced, surface tension decreases with the enhanced mutual solubility, and nonhydrocarbon components can react to compounds that are readily removed from the hydrocarbon mixture. The hydrocarbon mixture from the process is treated and upgraded to conventional hydrocarbon mixtures. Removal of solids, including fine particles, from effluents is possible in processes with near-critical and supercritical water.

Processing of biomass with water is an important topic since biomass is a renewable resource and usually contains a substantial amount of water. Therefore, processing of biomass with hydrothermal and supercritical water has an important role in the exploitation of this resource. It is treated in Chapter 8. Processing of biomass with high-temperature and supercritical water is carried out for different purposes: extraction and conversion for food purposes, derivation of useful compounds for chemical synthesis, acquiring compounds for fermentation, or transformation in order to use biomass for providing energy. In this respect, biomass is a renewable resource with low sulfur content and near-to-zero emission of CO_2 can be realized in the cycle of growing and conversion of biomass.

Biomass is a complex mixture of diverse compounds such as sugars, starch, cellulose, hemicellulose, lignin, and proteins. Investigation of the conversion of these compounds yields valuable information for processing natural materials that are mixtures of these compounds. Both aspects are discussed in Chapter 8.

The idea, to use as many compounds as possible from biomass, led recently to the vision of a biorefinery, in which the biomass feedstock is separated into all its valuable compounds. These compounds can be extracted, modified by hydrolysis or thermal pyrolysis, and then separated into gaseous, liquid, and solid fractions. Other ways to use biomass are liquefaction to a fuel-like liquid, or to gasify biomass to a gas that can be burnt or used as synthesis gas.

Another important topic of the future is the recycling of synthetic polymers. High-temperature and supercritical water are excellent reaction media for decomposition of synthetic polymers, since they do not introduce compounds that contaminate the products and water is easy to remove from the decomposition products. In Chapter 9, examples are discussed that illustrate the principles of depolymerization reactions with water.

Polymers from condensation polymerization processes, such as polyethylene terephthalate (PET), nylon, and polyurethane, are readily depolymerized to their monomers in supercritical water. Polymers from addition polymerization processes, such as phenol resin, epoxy resin, and polyethylene, can also be depolymerized in high-temperature and supercritical water. Composite polymer materials can be separated into useful fractions. Chlorinated polymers can be treated to remove halogens, beside the conversion of the polymers to useful degradation products. From biodegradable polymers, such as polylactic acid, the monomer can be recovered in high purity and yield.

Hydrothermal and supercritical water can be used for eliminating toxic and dangerous compounds by oxidation in an aqueous environment, see Chapter 10. Oxidation can be carried out as oxidation in a liquid aqueous environment in the temperature range from $T=100$ to 374 °C, as "Wet Air Oxidation," or as oxidation in supercritical water, known as "Supercritical Water Oxidation," and as oxidation in so-called "Hydrothermal Flames." These oxidation reactions aim for the conversion of the organic compounds to totally oxidized end-products or such effluents that can be further treated with conventional wastewater cleaning methods. For some applications, for example, for conversion of methane to methanol, partial oxidation is of interest. So far, success is limited in supercritical water, as presented in Chapter 10.

Processing of inorganic substances with high-temperature liquid and supercritical water is generally named "Hydrothermal processing" (Chapter 11). Hydrothermal processes can be used in the synthesis of fine particles, single crystals, functional metal oxides, and more. For many of these processes, subcritical water conditions are sufficient for the reaction. Processing in near-critical and supercritical water is attractive because the density, viscosity, diffusivity, and dielectric constant of the reaction medium can be controlled through relatively small changes in temperature and pressure. Variation of the properties of the reaction medium makes it feasible to control particle size, crystal structure, and morphology. Reaction at supercritical water conditions is a combination of hydrolysis, condensation, and thermal decomposition that can be at least partly also be controlled by adjustment of the operating conditions.

The interaction of aqueous solutions with the materials of the experimental or production plants can lead to major problems due to corrosion. The aqueous solutions contain many reactive compounds, for example, chloride ions, under oxidative or reductive conditions, that can cause corrosion. Corrosion includes all reactions of components of an aqueous reaction mixture with the walls of the equipment of experimental or production facilities, like pipes, valves, fittings, and autoclaves, as discussed in Chapter 12.

Corrosion in hydrothermal and supercritical water processes depends on the properties of the reaction mixture, on the properties of the construction materials, and on the construction of the processing equipment. In general, no satisfactory solution to corrosion problems can be achieved by addressing only one aspect. On the contrary, only a comprehensive adjustment of all aspects influencing corrosion can lead to a process configuration that can be operated successfully and for a reasonable, extended time span.

Various types of corrosion occur, such as general corrosion, intergranular corrosion, pitting corrosion, and stress corrosion cracking, as discussed in Chapter 12. General corrosion occurs mainly in the near-critical and supercritical temperature range in a region, where the density is high. Corrosion rates below $T=320\ °C$ are very low. At temperatures $T>320\ °C$ and pressures higher than the critical pressure, corrosion rates increase considerably. At a pressure of $P=24$ MPa, high corrosion rates drop down to the level observed at lower temperatures just around the critical temperature of water, while at a pressure of $P=38$ MPa, corrosion rates remain high up to a temperature of about $T=450\ °C$, since at that temperature density reaches the limit for corrosion due to ionic processes.

Processes with hydrothermal and supercritical water need a reaction vessel that can withstand the operating conditions. Although very similar in principle, the pressure vessels are different with respect to size, purpose, and construction, as discussed in Chapter 13.

Although, there are many different processes, as discussed in Chapters 4–11, the basic processing steps for hydrothermal and supercritical water systems are similar. They comprise the following: the feed has to be introduced into the high-pressure vessel, operating conditions have to be established and maintained, the process has to be carried out that leads to the desired products, the reaction products have to be retrieved and separated, and the water as the working fluid has to be recycled or cleaned for discharge. Obviously, differently designed components are needed for laboratory scale and for demonstration or production scale, although the basic process remains the same. At all sizes, the function of the components must be fulfilled. While at laboratory scale, the main effort is concentrated on the reaction, at larger scale new problems arise and need solutions, such as handling of feed and products in large quantities, heat transfer, fluid dynamics, and treatment of solids.

Experimental processes typically are concerned mainly with the process step itself. Handling of educt and product components is of secondary importance, as long as conditions are maintained for operating the process appropriately. Production processes are obviously operated to deliver products, contrary to experimental processes, for which the determination of optimal process parameters is the main objective and produced sample products are used for analysis and for presentation. In the context of this book, production processes are only treated to characterize the differences to experimental processes. No systematic compilation of production processes with hydrothermal and supercritical water is presented due to limitation of space.

It seems, at a first glance, that production processes differ from experimental processes mainly by size. While in experimental processes, samples of the size of less than grams to maximal kilograms are produced, production processes may begin at a production rate of hundreds of kilograms for very high-priced materials and may reach a yearly production rate of hundreds of thousands of tons. This difference in size brings along a number of problems, mostly engineering problems. Other problems to be solved are the supply of the feed and the disposal of wastes as the major logistic problems, financing as an economical problem, and acquiring acceptance for the process and the product as a sociological problem.

From the point of view of technology, the main difference between an experimental process and a production process is complexity. This means that solving a major processing problem with hydrothermal and supercritical water does not mean that a production process is established. Many more steps, some of them of totally other aspects than hydrothermal processing, become important, and in many cases are decisive. One of the aspects that make production processes much more complex than experimental processes is the necessity to treat the process fluid, water, in order to recycle it into the process or to dispose it into the environment. Examples for processes with hydrothermal and supercritical water are presented in Chapter 13.