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Fangming Jin *Editor*

Application of Hydrothermal Reactions to Biomass Conversion

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Fangming Jin
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Preface

The earth's sustainable development is threatened by energy exhaustion and rising atmospheric concentrations of carbon dioxide linked to global warming. One of the causes for energy crisis and increased atmospheric carbon dioxide could be the imbalance between the rapid consumption of fossil fuels in anthropogenic activities and the slow formation of fossil fuels. An efficient method for counteracting the imbalance in the carbon cycle should involve the rapid conversion of biomass and organic waste into fuels and chemicals. For this purpose, we can learn from the geologic formation of fossil fuels. It is known that hydrothermal reaction plays an important role in forming petroleum, natural gas, and coal from organic wastes, and thus can be recognized as another pathway in the carbon cycle.

Hydrothermal reaction is generally defined as a reaction occurring in the presence of an aqueous solvent at high temperature and high pressure. The application of hydrothermal reaction to the conversion of biomass, as a relatively new technology, is receiving increasing attention. It has been demonstrated that the hydrothermal conversion of biomass shows excellent potential for the rapid conversion of a wide variety of biomass into fuels and/or value-added products. It is because high-temperature water exhibits very different properties from ambient liquid water and is environmentally friendly due to the nature of the reaction medium, i.e., water. Thus, if the geologic formation of fossil fuels in nature could be combined with the hydrothermal methods being studied for biomass conversions, an efficient scheme could be realized to recycle carbon and produce fuels and/or chemicals.

This book compiles recent advances in hydrothermal conversion of biomass into chemicals and/or fuels and consists of 15 chapters. It introduces the properties of high-temperature water, the merits of hydrothermal conversion of biomass, and some novel hydrothermal conversion processes, such as hydrothermal production of value-added products (with an emphasis on the production of organic acids), hydrothermal gasification, hydrothermal liquefaction, and hydrothermal carbonization. A wide range of biomass and biomass waste is involved in this book, from carbohydrates, lignocelluloses, and glycerine, to bio-derived chemicals and sewage sludge.

This book will help readers to expand their knowledge of biomass conversion and the carbon cycle, and facilitate understanding of how the problems associated with biomass conversion, shortage of energy, and the environment, can be solved.

It is the editor's hope that materials compiled in this book will be useful in conveying a fundamental understanding of hydrothermal conversion of biomass in the carbon cycle so that a contribution can be made to achieving sustainable energy and environment.

Fangming Jin

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Part I

Characters of High Temperature Water and Hydrothermal Reactions

Chapter 1
Water Under High Temperature and Pressure Conditions and Its Applications to Develop Green Technologies for Biomass Conversion

Fangming Jin, Yuanqing Wang, Xu Zeng, Zheng Shen and Guodong Yao

Abstract This chapter introduces the chemical and physical properties of water under high temperature and pressure, such as ion product, density, dielectric constant and hydrogen bonding, and the applications of these properties on biomass conversion. These properties that are adjustable by changing the reaction temperature and pressure or adding additives are central to the reactivity of the biomass feedstock to break the C–C or C–O bonds. For example, glucose will follow different reaction pathways under acidic or alkali environment which is related to the ion product of water. Presently, hundreds of strategies utilizing these properties to transform biomass into target products intentionally or unintentionally are proposed. In this chapter, the hydrothermal processes applied in the conversion of biomass including cellulose, hemicelluloses, lignin and glycerin into commodity chemicals such as organic acids are mainly reviewed. In addition, the production of CO_2 as a byproduct from biomass conversion is sometimes inevitable. To achieve 100 % carbon yield, the process of reduction of CO_2 is often neglected but required. In the last section, the one pot reaction of glycerin conversion and CO_2 reduction is reviewed based on the hydrogen bonding property.

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1.1 Introduction

The terminology used in the literature for water under high temperature and pressure conditions (WHTP) is quite diverse. For instance, hot compressed water (HCW) is used to denote water above 200 °C and at sufficiently high pressure [1]. High temperature water (HTW) is also defined as liquid water above 200 °C [2]. Based on the critical point of water ($T_c = 373$ °C, $P_c = 22.1$ MPa), water can be divided into sub-critical water (below its critical point) and super-critical water (above its critical point). The lower limit of temperature of subcritical water can be 100 °C in the liquid state [3]. The terminology "near-critical water" is also often employed [4]. Aqueous phase processing (APP) is employed in the liquid water at 200–260 °C and 10–50 bar to produce H_2, CO, and light alkanes from sugar-derived feed [5]. More broadly and popularly, the terminology "hydrothermal", originally from geology, is used in the literatures to denote the reaction medium of high temperature and pressure water. According to their main product, it can be divided into hydrothermal carbonization (usually conducted at 100–200 °C) [6], hydrothermal liquefaction (often at 200–350 °C) [7], hydrothermal gasification (often at 350–750 °C) [8], Thus in this chapter, the terminology of hydrothermal will be mostly adopted to denominate water above 100 °C and 0.1 MPa including the sub and super-critical water.

The distribution of products from hydrothermal biomass conversion, such as gas, liquid or solid, is largely dependent on the properties of water at different states. Two competing reaction mechanisms are present: an ionic or polar reaction mechanism typical of liquid phase chemistry at low temperature and a free radical reaction mechanism typical of gas phase reactions at high temperature [9, 10]. The latter radical reactions are preferred to lead gas formation [11]. In addition, molecular reaction, which is different from ionic and radical reactions, is molecular rearrangement enhanced by coordination with water and proceeds around the critical region of water [12].

Therefore, in the following sections, we will introduce the representative properties of WHTP such as ion product, density, dielectric constant and hydrogen bonding, and discuss the effect of these properties on biomass conversion.

1.2 Ion Product

The ion product (K_w), also called self-ionization constant, is defined as the product of the concentrations of H^+ and OH^- in the water in units of mol^2/kg^2. When increasing the temperature, the ion product of water increases from $K_w = 10^{-14}$ mol^2/kg^2 at room temperature to approximately 10^{-11} mol^2/kg^2 at around 300 °C at constant pressure (250 bar) [2]. Above the critical temperature, the ion product decreases sharply with increasing temperature [2]. In the ranges when water has a bigger K_w number, water may show enhancement of acid and base catalyzed reactions due to the high concentration of H^+ and OH^- ions [7]. Furthermore, it is expected to get higher yield of target chemicals by adding minimal amounts of either acid or base catalysts. Antal et al. proposed that the ionic reaction are favored at $K_w > 10^{-14}$, and free radical reactions are favored at $K_w < 10^{-14}$ [13]. In this section, five classes of reactions, often taken place in the conversion of biomass, are discussed with one typical example to show the influence of ion product of water in the acid or base catalyzed reaction.

1.2.1 Hydrolysis

As shown in Fig. 1.1, hydrolysis is one of the major and usually initial reactions happened in conversion of biomass in which glycosidic bonds between sugar units are cleaved to form simple sugars such as glucose and partially hydrolyzed oligomers. Hydrolysis can happen both in acid and base catalyzed reactions, while the former reaction condition (acidic) is more often adopted because base catalysis lead to more side reactions [14, 15]. The hydrolysis of cellulose to glucose is a widely investigated reaction in biomass conversion because cellulose is the major component of plant biomass and the product glucose is a very important intermediate [16]. Under hydrothermal conditions, cellulose reacts with water and is hydrolyzed into glucose or other monomers proceeding through C–O–C bond cleavage and accompanied by further degradation. Three possible reaction paths of cellobiose hydrolysis are demonstrated including acid, base and water catalyzed ways [15]. Acid hydrolysis proceeds through the formation of a conjugated acid followed by the glycosidic bond cleavage and leads to the two glucose units. In the base pathway, the OH^- attacks at the anomeric carbon atom, renders the cleavage of the O bridge and again yields the two glucose units. The water catalyzed reaction is characterized by H_2O adsorption. Then water and the glycosidic bond split simultaneously and form two glucoses again. Sasaki et al. [17, 18] conducted cellulose decomposition experiments with a flow reactor type reactor from 290 to 400 °C at 25 MPa. Higher hydrolysis product yields (around 75 %) were obtained in supercritical water (SCW) than in subcritical water. The reason was attributed to the difference of reaction rate in the formation and degradation of oligomer or glucose. At a low temperature region, the glucose or oligomer conversion rate was much faster than the hydrolysis rate of cellulose. However, around the critical point, the hydrolysis rate jumped to more than an order of magnitude higher level and became faster than the glucose or oligomer decomposition rate. The direct observation by diamond anvil cell showed that the cellulose disappeared with a more than two orders of magnitude faster rate at 300–320 °C than that estimated [18]. This phenomenon indicated that the presence of a homogeneous hydrolysis atmosphere caused by the dissolution of cellulose or hydrolyzed oligomers around the critical temperature and thus resulted in the high cellulose hydrolysis rate. The additional acid catalysts including homogenous and heterogenous catalysts would

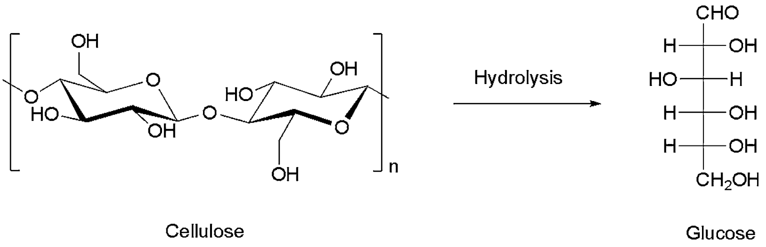


Fig. 1.1 Hydrolysis of cellulose

also enhance the yield of glucose which was around 50–80 % [16]. The base catalyst might cause more side reactions [15] but could inhibit the formation of char which was very crucial in the continuous flow reactor to prevent plug [19].

1.2.2 *Isomerization*

As shown in Fig. 1.2, the isomerization between glucose and fructose is very common and has been considered as one key step in biomass conversion. The difference of their reactivity and selectivity for target materials makes the tunable transformation to specific one (usually from glucose to fructose) highly desirable [20]. This reaction is typically catalyzed by the base catalyst, named as Lobry de Bruyn-Alberda van Ekensterin transformation (LBAE). The mechanism proceeds by deprotonation of alpha carbonyl carbon of glucose by base, resulting in the formation of a series of enolate intermediates. The overall process involves hydrogen transfer from C2 to C1 and from O2 to O1 of an alpha hydroxy aldehyde to form the corresponding ketone. Kabyemela et al. [21] found the isomerization from fructose to glucose is negligible compared with its reversion under hydrothermal conditions because glucose and fructose have same product distribution except for 1,6-anhydroglucose which is not observed in the decomposition of fructose. Recently, Davis et al. [22] reported another Lewis acid catalyzed pathway of isomerization via intramolecular hydride transfer for glucose–fructose. In addition to glucose–fructose isomerization, there is another important isomerization between glyceraldehydes and dihydroxyacetone under hydrothermal conditions [23].

1.2.3 *Dehydration*

Dehydration reactions of biomass comprise an important class of reactions in the area of sugar chemistry. As shown in Fig. 1.3, fructose can be dehydrated into hydroxymethylfurfural (HMF) with loss of three water molecules by acid

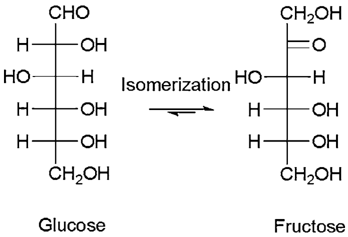


Fig. 1.2 Isomerization between glucose and fructose

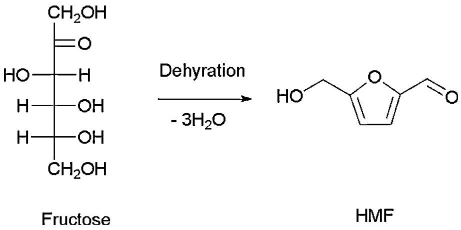


Fig. 1.3 Dehydration of fructose into HMF

catalyzed reaction. Antal et al. [24] proposed that HMF is produced from fructose via cyclic intermediates. Recent studies confirmed that the HMF formation was from the acid-catalyzed dehydration of C6-sugars in the furanose form [25, 26]. Hence, fructose which contains 21.5 % of furanose tautomers in aqueous solution can be converted to HMF easier than glucose which contains only 1 % of furanose tautomers in aqueous solutions. The rehydration of HMF with two molecules of water would produce levulinic acid and formic acid [27]. Levulinic acid can be further converted into g-valerolactone (GVL) via hydrogenation with hydrogen [28], which can be converted to liquid alkenes in the molecular weight range appropriate for transportation fuel [29].

Yoshida et al. obtained the best yield of HMF (65 %) from fructose achieved at a temperature of 513 K for a residence time of 120 s [30]. Since glucose is more common than fructose in biomass conversion, researchers usually adopt a two-step strategy to produce HMF from glucose: (1) isomerization of glucose into fructose catalyzed by base and (2) dehydration of fructose into HMF by acid [31]. Since water under high temperatures and pressures can play the roles of both acid and base catalysts, high yield of HMF can be obtained under hydrothermal conditions in one step. Jin et al. [32] reported the total highest yields of HMF and levulinic acid from glucose were about 50 %, which occurred at 523 K for 5 min with H_3PO_4 as a catalyst and the highest yield of levulinic acid was about 55 % at 523 K for 5 min with HCl as a catalyst. For the three mineral acids (HCl, H_2SO_4 and H_3PO_4), it was found that not only the pH, but also the nature of the acids, had great influence on the decomposition pathway [30]. The order for the production of HMF using the three acids was in the sequence of $H_3PO_4 > H_2SO_4 > HCl$ [32]. On the contrary, the order for production of levulinic acid followed $HCl > H_2SO_4 > H_3PO_4$ [32].

There are some drawbacks in the acid catalyzed formation of HMF from fructose or glucose. Kinetics studies [33–35] showed that humins formation from glucose and HMF cannot be neglected. The activation energy of its formation from glucose and HMF were estimated at 51 and 142 kJ/mol, respectively, while dehydration of glucose to HMF and rehydration of HMF to levulinic acid were 160 and 95 kJ/mol, respectively [35]. To minimize the formation of humins and enhance the selectivity towards HMF, a biphasic solution with water and organic phase was adopted that would continuously extract HMF as it is produced [36–39]. Dumesic et al. reported a 61 % yield of HMF from glucose using a biphasic reactor of water/tetrahydrofuran with $AlCl_3 \cdot 6H_2O$ catalyst at 160 °C [37].

1.2.4 Retro Aldol Reaction

Many researchers [17, 21, 23, 40, 41] have examined intermediate products for the hydrothermal degradation of glucose and cellulose at a reaction temperature of near 300 °C. As shown in Fig. 1.4, through these studies, it was revealed that some compounds containing three carbon atoms, such as glyceraldehyde, dihydroxyacetone and pyruvaldehyde, were formed by the base catalytic role of HTW. Furthermore, there was isomerization occurring between glyceraldehyde and dihydroxyacetone followed by their subsequent dehydration to pyruvaldehyde [23]. The ketone (fructose) can undergo reverse aldol reaction by C3–C4 bond cleavage to form glyceraldehydes. These C3 carbon compounds were considered as the precursors of lactic acid from transformation of pyruvaldehyde [40]. On the other hand, the intermediates glycoaldehyede and erythrose were transformed from glucose by retro aldol reaction [17, 21]. In Organic Chemistry, retro aldol reaction can usually be catalyzed by either an acid or a base. Experimental data suggested, however, that retro aldol reaction under hydrothermal conditions was base-catalyzed [2]. Sasaki et al. [42] reported that the retro aldol reaction selectively proceeded at higher temperatures (above 673 K) and lower pressure (below 25 MPa). At a low temperature, the retro aldol reaction was preferred in alkali environment [43].

These formed intermediates from C2–C3 or C3–C4 bond cleavage by reverse aldol reaction from hexoses can then be fast transformed into mainly lactic acid and other low molecular acid in which glyceraldehyde can produce a higher yield of lactic acid [41]. Lactic acid is a key chemicals as a building block for biodegradable lactic acid polymers with limited environmental impact. Jin et al. [44, 45] showed that the addition of base catalyst [NaOH and $Ca(OH)_2$] can increase the yield of lactic acid. The highest yield of lactic acid from glucose was 27 % with 2.5 M NaOH and 20 % with 0.32 M $Ca(OH)_2$ at 300 °C for 60 s [44]. A very recent study by Labidi et al. [46] also found that the highest yield lactic acid of 45 % from corn cobs was obtained using 0.7 M $Ca(OH)_2$ at 300 °C for 30 min. The reason that base catalyst increased the yield of lactic acid can be attributed to the enhancement of reaction pathway for lactic acid production discussed above.

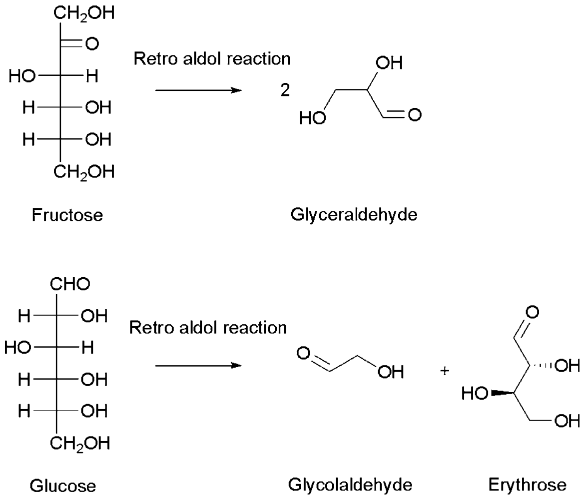


Fig. 1.4 Retro aldol reaction of fructose and glucose

Another reason may be that the lactate formed actually by alkaline solution prevents it from decomposition [47]. Compared with NaOH at lower alkaline concentration [44], $Ca(OH)_2$ promoted more effectively the production of lactic acid than NaOH at the same OH^- concentration. It is probably because Ca^{2+} was more capable than Na^+ in forming complexes with two oxygen atoms in the hexoses. When the concentration of $Ca(OH)_2$ increased from 0.32 to 0.4 M, it did not lead to increase in lactic acid yield; while the optimum OH^- concentration for NaOH was 2.5 M. This difference can be attributed to the fact that the saturated solubility of NaOH is higher than that of $Ca(OH)_2$.

1.2.5 Decarboxylation and Decarbonylation

$$[\mathrm{HCOOH} \rightarrow \mathrm{H_2} + \mathrm{CO_2}(\text{decarboxylation})] \tag{1.1}$$

$$[\mathrm{HCOOH} \rightarrow \mathrm{H_2O} + \mathrm{CO}\ (\text{decarbonylation})] \tag{1.2}$$

The reactions of formic acid play a key roles in the chemistry of hydrothermal reaction partly because it was the simplest acid and product of many acid/base catalyzed or oxidation reactions, and partly because itself or formate is considered to be the intermediate of water gas shift reaction and reduction of carbon dioxide [48]. The understanding of its reactivity especially coupled with the properties of water will facilitate the researches on energy production and environment protection. As shown in Eqs. 1.1 and 1.2, for the decomposition of formic acid, there existed two competitive pathways: decarboxylation and decarbonylation. Early experimental results showed that in the gas phase the decarbonylation dominated, but in the liquid phase the decarboxylation dominated [49, 50]. Savage et al. [49]

conducted the formic acid decomposition experiments from 320 to 500 °C, at pressures from 18.3 to 30.4 MPa, and at 1.4–80 s reaction times. Conversion rates ranging from 38 to 100 % were obtained with the major products of CO_2 and H_2. In their experiments, the decarbonylation product CO was also detected and the yields were always at least an order of magnitude lower than the yields of decarboxylation. The reason why decarboxylation dominated in the liquid phase can be explained by the presence of water as a homogeneous catalyst that can catalyze decarboxylation more than decarbonylation by a theoretical calculation [51]. The kinetic data also supported the assumption of a homogenous reaction based on the consistency with the reaction rate law that was first order in formic acid [49]. However, Nakahara et al. [52] indicated that the reactor wall might show catalytic role in the formic acid decomposition that is a heterogeneous reaction according to an NMR investigation. Compared with its acidic environment, Jin et al. [47] found the addition of alkali could prevent the formic acid decomposition even with the presence of oxidant H_2O_2 at 250 °C for 60 s.

1.3 Water Density

Water density can be varied greatly with temperature and pressure under hydrothermal conditions. Water density decreases with the increase in temperature at constant pressure. For example, water density decreases from about 800 kg/m^3 like liquid phase to about 150 kg/m^3 like gas phase without phase change as the temperature increases from 300 to 450 °C. Meanwhile, water density controlled by temperature and pressure can be related to ion product by Eq. 1.3 using a fitting method proposed by Marshall et al. [53].

$$[\log K_w = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + (E + \frac{F}{T} + \frac{G}{T^2}) \log \rho] \tag{1.3}$$

where T is temperature in Kelvin, ρ is density in g/cm^3, and A–G are fitting parameters. This result indicated that the chemistry of biomass conversion can also be controlled by water density. However, it is not to say that water density affects the reaction mechanism only by changing ion product of water. Water density changes can reflect the changes of water in molecular level such as solvation effect, hydrogen bonding, polarity, dielectric strength, molecular diffusivity and viscosity that will influence the chemistry inside [54]. In super-critical water, the reaction mechanism varies from a reaction atmosphere that favors radical reaction to one that favors ionic reactions dictated by the water density [55]. Experimental data showed that reactions seemed to proceed via ionic pathways in the high density water while radical reactions seemed to be the main reaction pathways in the less dense super-critical water [9]. Westacott et al. [56, 57] investigated *tert*-butyl chloride dissociation in super-critical water by computational methods and showed that water density affect the competition between ionic and radical reaction mechanisms. The ionic heterolytic dissociation was preferred over the radical homolytic dissociation when water density was larger than 0.03 g/cm^3 [56, 57]. In this section, different reaction mechanisms via ionic or radical pathways affected by water density were introduced from different feedstock.

1.3.1 Cellulose

Aida et al. [58, 59] examined the reactions of D-glucose and D-fructose under high temperature (up to 400 °C) and pressure (up to 100 MPa) water. The benzilic acid rearrangement reaction from pyruvaldehyde to lactic was enhanced by the water density [59]. And the dehydration reaction to 5-HMF and the hydrolysis of 5-HMF were both enhanced by the increase in water density at 400 °C [58]. One explanation for the enhancement of water density was that water can lower the activation energy by forming "water bridge" in the transition state [51] and thus the increased water concentration would be advantageous for this effect. Another explanation for the density effect on the dehydration and hydrolysis reactions may due to the change in of ion product of water like mentioned above.

1.3.2 Glycerin

Glycerin, as a byproduct of biodiesel formation, can be a promising feedstock for chemicals and fuel production with hydrothermal treatment. The main product of glycerin degradation under hydrothermal conditions could be acrolein, acetaldehyde, formaldehyde, propionaldehyde, allyl alcohol, methanol, ethanol, lactic acid, carbon monoxide, carbon dioxide and hydrogen based on reaction conditions [9, 60–62]. Buhler et al. [9] conducted glycerin degradation experiments in near and super-critical water in the temperature range of 622–748 K, at pressures of 25, 35, or 45 MPa. They found a great change in the product composition with pressure (density) indicating the presence of different reaction mechanisms (ionic and radical reaction). The relative yield of acetaldehyde and formaldehyde increased with the increase in pressure (increase in water density) while that of methanol and allyl alcohol decreased. They suggested that acetaldehyde and formaldehyde were formed by ionic reactions and the latter by radical reactions. The relative stable yield of acrolein with pressure showed that both mechanisms were present.

1.3.3 Lignin

Lignin, the second most abundant polymeric aromatic organic substance in wood biomass after cellulose, has been considered as an important alternative source of chemical compounds. Wahyudiono et al. [63–65] performed lignin and its model compound decomposition experiments under hydrothermal conditions. The yields of catechol, phenol and *o*-cresol from guaiacol increased with increasing water density from 0.17 to 0.60 g/cm^3 at 653–673 K and at 25–40 MPa [63]. The results suggested that the increase in water density could enhance the hydrolysis of guaiacol into its derivatives and the dehydration of alcohols [63]. Sato et al. [66] reported that the yield of gas products from the gasification of alkylphenols can be increased with the increase in water density from 0 to 0.3 g/cm^3 in SCW at 673 K. Osada et al. [67] compared the gas yield from lignin and 4-propylphenol which is a model of low-molecular weight compounds from lignin at 673 K with water density from 0.1 to 0.5 g/cm^3. The results indicated that the step (decomposition of lignin to low-molecular weight compounds) in the gasification was enhanced by increasing the water density, and the rate of gasification of 4-propylphenol was not affected by water density.

1.3.4 C_1 Compounds

Formaldehyde is very reactive under hydrothermal conditions. Because two formaldehyde molecules can produce methanol and formic acid by Cannizzaro reaction, and one formaldehyde can decompose into carbon monoxide and hydrogen. The product of carbon monoxide with H_2O can further produce carbon dioxide and hydrogen by water gas shift reaction. The produced formic acid will undergo competitive pathways to produce CO_2 or CO like mentioned above. Osada et al. [68] discussed the water density (0.17–0.50 g/cm^3) dependence of formaldehyde reaction in super-critical water with batch experiments. It was found that the Cannizzaro reaction mechanism was the preferred reaction pathway for formaldehyde with the product of methanol at higher water densities. At lower water densities, monomolecular decomposition became the main reaction pathway with higher yield of carbon monoxide. The water density dependence on rate constant of formic acid disappearance at super-critical water was studied by Yu et al. [49]. It was found that the rate constant of formic acid disappearance increased with increasing of the water concentration from 5 to 10 mol/L, then decreased, and then increased again when water concentration was greater than 25 mol/L. As the water concentration increased from 1.8 to 5.7 mol/L in super-critical water at 500 °C, the OH radical was proposed to increase which promoted the oxidation of methanol [69].

1.4 Dielectric Constant

The dielectric constant is the ratio of the permittivity of a substance to the permittivity of free space. The dielectric constant of water under ambient condition is 78.5. Water under this condition could be used as good solvent for the polar

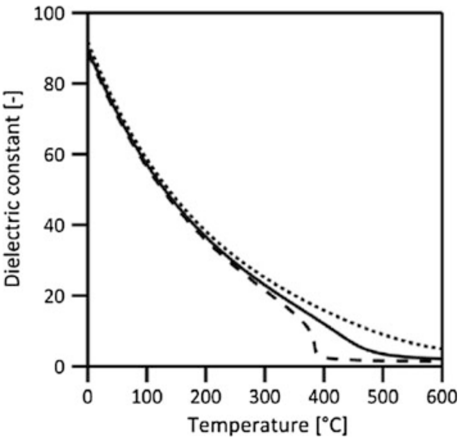


Fig. 1.5 Dielectric constant of water as a function of temperature. *Dashed line* 25 MPa; *solid line* 50 MPa; *dotted line* 100 MPa. Reprinted from Ref. [70], Copyright 2013, with permission from Elsevier

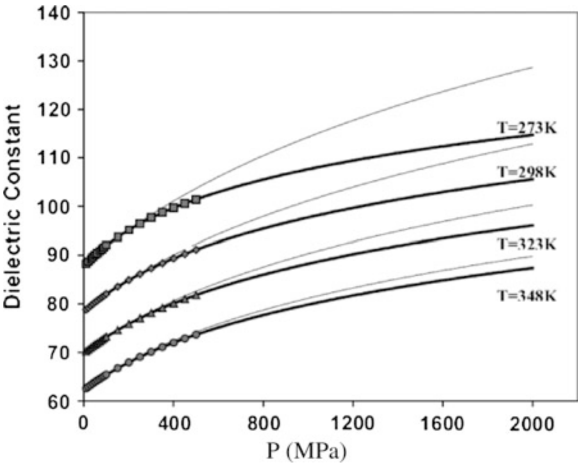


Fig. 1.6 Dielectric constant of water as a function of pressure at constant temperatures (273, 298, 323 and 348 K) (*fine lines* Bradley's equation [72]; *thick lines* adjusted values extracted from the *International Association for the Properties of Water and Steam* [73]). Reprinted with the permission from Ref. [72]. Copyright 1979 American Chemical Society

materials. However, it cannot be used to dissolve hydrocarbon and gas. Dielectric constant of water as a function of temperature can be seen in Fig. 1.5 [70]. As shown in Fig. 1.5, the dielectric constant of water reduces sharply with the increase of temperature of water. HTW in sub-critical and super-critical condition behaves like many organic solvents which can dissolve organic compounds completely forming a single fluid phase. The advantages of a single supercritical phase reaction medium are that higher concentrations of reactants can often be attained and no interphase mass transport processes which will hinder the reaction rates were indispensable.

As a consequence of this lack of data, attempts to estimate the properties of aqueous species at high temperature and/or high pressure rely on the estimated or extrapolated dielectric constant values [71]. The dielectric constant dependence on the pressure, proposed by Bradley and Pitzer [72], can be seen in Fig. 1.6. Bradley used an equation suggested by Tait in 1880 for volumetric data. As shown in figure1.6, at constant temperature, the dielectric constant values increased linearly with the increase of pressure. It should be noted that the original Bradley's equation does not reproduce adequately the data available from the *International Association for the Properties of Water and Steam* [73] used in Fig. 1.6 for P above 400 MPa, particularly at and above 323 K. However, the trends are similar, which can approximately represent the change of dielectric constant with different pressure.

1.4.1 Dielectric Constant of High Temperature Water

Park et al. compared the dielectric constant (ε) of superheated water at different temperature and pressure, as shown in Table 1.1 [74]. The dielectric constant values of water decreased with the increase of temperature from 44 at 150°C to 2 at 350 °C. These values are between those of organic solvent ethanol ($\varepsilon = 24$ at 25 °C) and methanol ($\varepsilon = 33$ at 25 °C). This indicates that superheated water can be used as an organic solvent. Moreover, superheated water is readily available, non-toxic, reusable and very low in cost as well as environmentally friendly. Therefore, superheated water can be used as an alternative cleaning technology, instead of using organic solvents or toxic and strong aqueous liquid media. For the extraction of dioxins [75], pesticides [76], PCBs [77], and PAHs [78]. Lagadec et al. reported that the optimum subcritical water extraction was at 275 °C in 35 min for all low and high molecular weight PAHs from contaminated Manufactured Gas Plant (MGP) soil [76]. Moreover, it can also be used to determine a superior instant analytical technique (using GC oven as heater) by using organic solvent [78]. However, a complete extraction technology with shorter extraction time at a temperature range (from 100 to 300 °C) using subcritical water for industrial application has not been determined; therefore, an additional study is necessary [74].

The dielectric constant of SCW is very special, because the dielectric constant under this condition is much lower, and the number of hydrogen bonds is much smaller and their strength is much weaker. Supercritical water above 374 °C and 221 bar shows water is greatly diminished-frequently less than reduced local molecular ordering and less effective hydrogen bonding as characterized by its lower dielectric constant (about 1 to 3) [79]. As a result, SCW behaves like many organic solvents so that organic compounds have complete miscibility with SCW. Moreover, gases are also miscible in SCW, thus a SCW reaction environment provides an opportunity to conduct the chemical reactions in a single fluid phase that would otherwise occur in a multiphase system under conventional conditions [80]. Therefore, SCW exhibits considerable characters of solvent, which can dissolve nonpolar materials and gas, and the characters of easy diffusion and motion [81]. The dielectric constant of SCW corresponds to the value of polar solvent under ambient condition. The dielectric constant of ambient water varies continuously over a much larger range in the supercritical state. This variation offers the possibility of using pressure and temperature to influence the properties of the reaction medium. Therefore, it is possible for the formation of C–C bond

Table 1.1 Dielectric constant (ε) of subcritical water and common organic solvent

ε (at subcritical water °C)	ε of common organic solvent at 25 °C
44 (150)	1.9 (n-hexane)
35 (200)	21 (acetone)
27 (250)	24 (ethanol)
20 (300)	33 (methanol)
2 (350)	39 (acetonitrile)

Table 1.2 Dielectric constant and density of water at some supercritical conditions

Temperature (°C)	Pressure (MPa)	Density (g/cm^3)	Dielectric constant
400	25	0.17	2.4
400	30	0.35	5.9
500	25	0.09	1.5
500	30	0.12	1.7
350	25	0.63	14.85

with organ metallic catalytic reactions which always needs organic solvent. Gomez-Briceno et al. compared the dielectric constant of water at different supercritical conditions, 400 and 500 °C and two pressures values, 25 and 30 MPa, as shown in Table 1.2 [82]. The data showed that the dielectric constant decreased significantly with the decrease of temperature. However, the influence was very small.

Water with large dielectric constant will exhibited strong effect with microstructure of water, and eventually influence the reaction [1]. The large dielectric constant means that substances whose molecules contain ionic bonds tend to dissociate in water yielding solutions containing ions. This occurs because water as a solvent opposes the electrostatic attraction between positive and negative ions that would prevent ionic substances from dissolving. These separated ions become surrounded by the oppositely charged ends of the water dipoles and become hydrated. This ordering tends to be counteracted by the random thermal motions of the molecules. Water molecules are always associated with each other through as many as four hydrogen bonds and this ordering of the structure of water greatly resists the random thermal motions. Indeed it is this hydrogen bonding which is responsible for its large dielectric constant.

1.4.2 Effects of Dielectric Constant on the Application of High Temperature Water

In this section, different reaction mechanisms affected by dielectric constant of HTW are introduced.

(1) Hydrolysis of organic compounds

Townsend studied the relationship between the hydrolysis rate constants and the dielectric constant, and the results showed that the hydrolysis rate constants correlated well with the dielectric constant of water [83]. Marrone and Tester also have studied the hydrolysis of methylene chloride to form formaldehyde and HCl [84, 85]. Their research results showed that the dielectric constant of the reaction medium influenced the rate of hydrolysis significantly. The reaction slowed down as the temperature increased along with the decrease of dielectric constant of water. With higher dielectric constant, the intermediates were stabilized much better and the hydrolysis reaction was accelerated. Marrone has developed a quantitative kinetics model and showed that more accurately with experimental data [86], as shown in Fig. 1.7. From Fig. 1.7, it can be seen that in the subcritical region where water is still quite polar, the rate constant is small; however, in the range of temperatures just beyond the critical point where dielectric constant drops by an order of magnitude, the rate constant increases dramatically. These researches showed that in the process of hydrolysis, the reaction rate could be regulated by the dielectric constant via the change of temperature.

(2) Hydrothermal conversion of carbohydrate biomass

The hydrothermal process is one of the most promising processes for the conversion of carbohydrate biomass into chemicals, because HTW has unique properties as a reaction medium, such as a lower dielectric constant, fewer and weaker hydrogen bonds [2, 4]. By the variation of the relative dielectric constant with temperature and pressure, reaction rates can be controlled. There have been extensive researches on the conversion of biomass into chemicals under hydrothermal conditions. Sasaki et al. studied the hydrothermal conversion of guaiacol in sub- and SCW [87]. Results showed that the reaction rate constant was different with the change of temperature, which was related to the dielectric constant, as shown in Fig. 1.8.

Ragauskas et al. reviewed the application of high temperature water [88]; for example, near-critical water (200–300 °C) exhibited a reduction in dielectric constant (20 to 30) relative to ambient water, and the ability of HTW to dissolve both nonpolar organic molecules and inorganic salts was comparable to that of the popular organic solvent acetone. Fangming Jin performed a series of studies on the hydrothermal conversion of biomass and CO_2 due to the unique characters of HTW including the dielectric constant [7, 89–91]. These results showed that the lower dielectric constant, caused by the high temperature, affected the reaction significantly, which induced the effective conversion of biomass and CO_2 gas under hydrothermal conditions. Franck et al. studied the cellulose conversion with solid acid catalyst in supercritical state, which showed that the dissolution of nonpolar organic macromolecules such as cellulose was accelerated with low dielectric constant [92].

Fig. 1.7 Water dielectric constant as a function of temperature. Reprinted with the permission from Ref. [86]. Copyright 1998 American Chemical Society

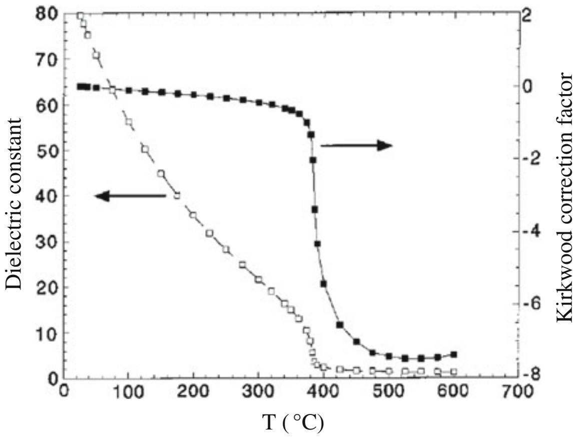
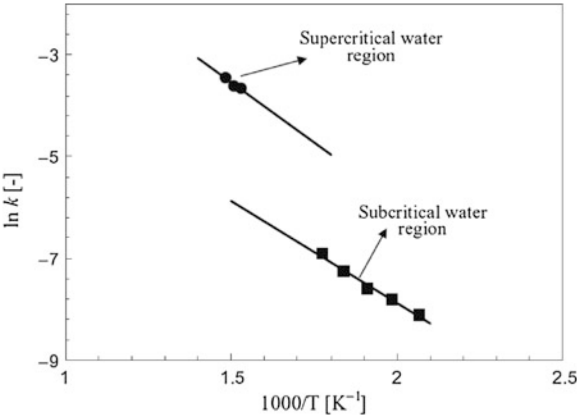


Fig. 1.8 Rate constants of guaiacol conversion in subcritical water (at 483–563 K, 8 MPa: *squares*) and supercritical water (at 653–673 K, 30 MPa) Reprinted from Ref. [87], with permission from Springer Science+Business Media



(3) Degradative extraction

Morimoto et al. has studies the miscibility of SCW with asphaltene at 400–450 °C and 20–35 MPa [93]. Relationship between extraction yield and pressure, dielectric constant can be seen in Fig. 1.9. With increasing the pressure at 440 °C, the degradative extraction yield of AS using SCW reached a maximum at around 30 MPa. The extraction behavior was thought to be controlled mainly by the water properties represented by the dielectric constant and Hansen solubility parameter. supercritical water extraction at >400 °C and >25 MPa has been used in several types of heavy crude, including oil sand bitumen [94], vacuum residue [95], asphalt [96], heavy oil [97], and coal tar [98]. Wang et al. reviewed the conventional Soxhlet extraction and the new alternative methods used for the extraction of nutraceuticals from plants [99]. The microwave-assisted extraction depends on the dielectric susceptibility of solvent and matrix, better recoveries can be obtained by moistening samples with a substance that possesses a relatively high dielectric constant such as water.

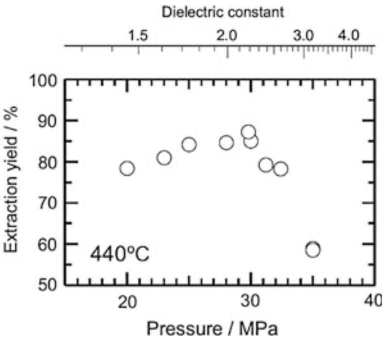


Fig. 1.9 Relationship between extraction yield and pressure (the extra scale above: dielectric constant of pure water at each) Reprinted from Ref. [93], Copyright 2012, with permission from Elsevier

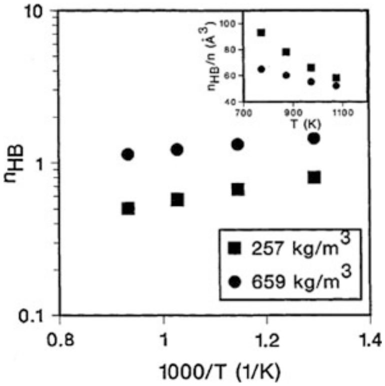


Fig. 1.10 Number of hydrogen bonds per water molecules. Reprinted with the permission from Ref. [100]. Copyright 1996 American Chemical Society

1.5 Hydrogen Bonding

WHTP exhibits properties that are very different from those of ambient liquid water, but hydrogen bonding is the source of many unique properties of liquid water.

It can be shown in Fig. 1.10 that with increasing temperature and decreasing density, the hydrogen bonding in water becomes weaker and less persistent [100]. For example, water at 673 K and 0.5 g/cm^3 retains 30–45 % of the hydrogen bonding that exists at ambient conditions, whereas water at 773 K and 0.1 g/cm^3 retains 10–14 % [101]. The hydrogen bonding network in ambient liquid water exists in the form of infinite percolating large clusters of hydrogen-bonded water molecules, but the hydrogen bonding network in WHTP exists in the form of small clusters of hydrogen-bonded water molecules [100, 102–104]. In general, the average cluster size of hydrogen-bonded water molecules decreases with increasing temperature and decreasing density. For instance, most of the clusters at 773–1073 K and 0.12–0.66 g/cm^3 consist of five water molecules or less, although existing a small number of clusters that are as large as about 20 water molecules [100, 103, 104]. These results shows that the less hydrogen bonding results in much less order in WHTP than ambient liquid water, and then individual water