CHAPTER II

FUNDAMENTAL THEORY

2.1 Introduction

When an aqueous solution/dispersion of a carbohydrate (e.g., glucose, sucrose, starch, etc.) is heat-treated at a moderate temperature in the 170–350°C range (under pressure), a carbon-rich black solid is obtained as insoluble product [26]. This process, which will be termed hydrothermal carbonization, gives rise to other substances besides the solid residue [26]. These include aqueous soluble products (furfural, hydroxymethylfurfural, acids, and aldehydes) and small amount of gases (CO_2, CH_4, etc.) [27]. In the present work our primary interest is the carbonaceous solid product. The first research work on the hydrothermal carbonization of carbohydrates was carried out during the first decades of the 20th century with the aim of understanding the mechanism of coal formation. Thus, in 1913 Bergius and Specht subjected cellulose to hydrothermal carbonization at temperatures in the 250–310°C range, as a result of which they obtained a black residue with a O/C atomic ratio of 0.1–0.2 (O/C atomic ratio of cellulose: 0.84) [17]. Later, in 1932, Berl and Schmidt investigated the hydrothermal treatment of cellulose over a wider temperature range (200–350°C) [28]. In 1960, van Krevelen et al. noticed that the solid products derived from the hydrothermal treatment of the cellulose and glucose have the same composition, which suggests that the hydrolysis products for both substances are similar [29]. In relation to this process van Krevelen proposed an H/C versus O/C diagram to analyze the chemical transformations that take place during the hydrothermal carbonization of these substances [29]. Renewed interest in the hydrothermal carbonization of saccharides has recently been established. However, the objectives of these new investigations are completely different to those previously mentioned. Now the main purpose is to use this process as a way to produce carbonaceous materials with specific properties (i.e., shape, size, chemical functionalities, etc.). In 2001, Wang et al. reported the synthesis of carbonaceous microspheres of a tunable size (in the 0.25–5.00 μm range) through the hydrothermal carbonization of sucrose at 190°C. Much attention has also been focused on the hydrothermal carbonization of sugars in the presence of inorganic salts, which gives rise to the formation of hybrid carbon/metal materials (C/Ag, C/Cu, C/Au, C/Pd, and C/Te), with complex nano-architectures [22]. In addition, the microspheres resulting from the hydrothermal carbonization have been employed as sacrificial templates for fabricating hollow spheres of inorganic compounds (Ga_2O_3, GaN, WO_3, SnO_2, etc.) [21]. Recently, Yao et al investigated the mechanism of formation of carbonaceous microspheres in the course of the hydrothermal treatment of glucose and fructose at low temperatures (120–160°C) [30].

2.2 Hot compressed water as the reaction medium

A phase diagram of water is shown in Figure 2.1 indicating a critical point of water at 374°C and 22.06 MPa [31]. With an increase in the temperature and pressure along the liquid-vapor saturation line, the density of the liquid phase gradually decreases; on the other hand, the density of the vapor phase gradually increases. The point at which the density of both phases become identical ($\rho_c = 322$ kg/m^3) is defined as the critical point. At this point, the phase boundary between two phases disappears and the water acts as the single fluid [32]. Above the critical point is the supercritical water. The subcritical water, on the other hand, exists at the pressure and temperature lower than the critical values [33].

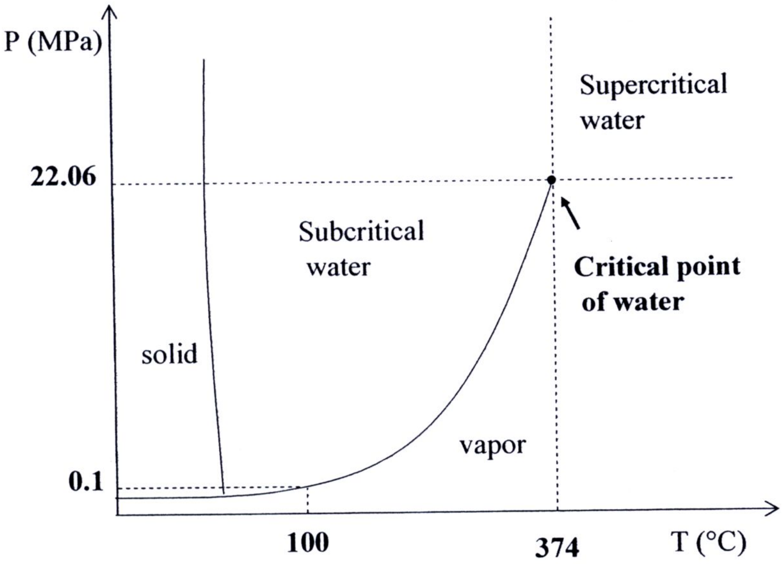

Figure 2.1 Phase diagram of water [32]

The subcritical and supercritical water has been applied for many chemical reactions and synthesis as the reaction medium, especially in the field of biomass utilization. This is due to an advantage of a wide range of properties, which are obtained only by changing the temperature and pressure. The dielectric constant (ε) and ion product of water (K_w) as a function of temperature at a constant pressure (25 MPa) are shown in Figure 2.2. In the subcritical region, the ion product increases up to three orders of magnitude higher than that in the ambient condition [34]. The ionic-type reactions, therefore, are being catalyzed by the H^+ and/or OH^- ions from the water dissociation without any addition of acid/base catalysts [35]. The reaction under subcritical condition, therefore, is the environmentally-friendly system. The ionic reactions include the hydrothermal pretreatment of lignocellulosic biomass [36]. In this reaction, the cellulose, hemicellulose, polysaccharide, and protein are hydrolyzed to yield their monosaccharides and smaller compounds (e.g., glucose, xylose, amino acids, and organic acids), which are utilized further as the bio-chemicals and bio-ethanol [28]. As approaching the critical point, the ion product and dielectric constant decrease dramatically [37]. The water turns into the nonpolar-like solvent with the high solubility of the organic compounds and gases. The ionic reaction, thus, is demoted and the radical reaction is enhanced instead, indicating that the reaction pathway can be controlled by manipulating the water conditions.

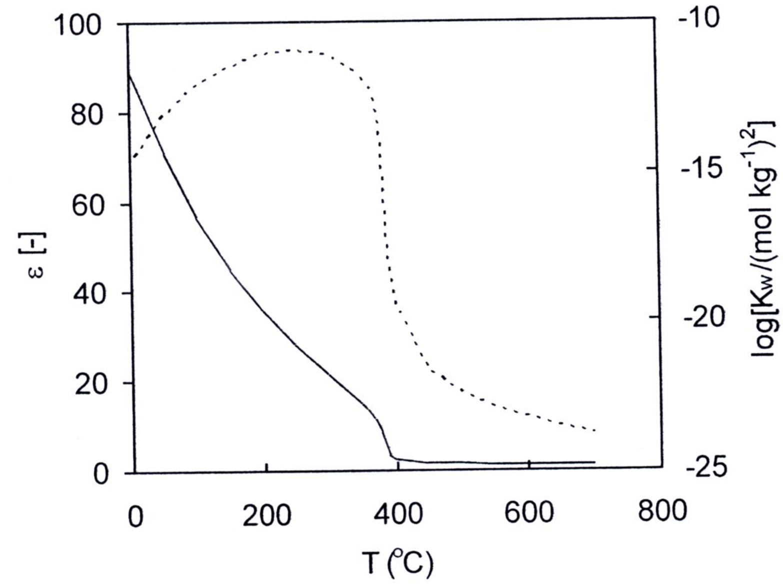

Figure 2.2 Dielectric constant (ε) and ion product of water (K_W) as a function of temperature at 25 MPa [31]