Basic Characteristics and Application Progress of Supercritical Water

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Abstract. Compared with water at normal temperature and normal pressure, supercritical water had large differences and also had some unique characteristics. In this paper, some basic physical properties of supercritical water, included density, viscosity, thermal conductivity, dielectric constant, ion product, hydrogen bond, diffusion coefficient and solubility, were introduced. Some applications of supercritical water oxidation technology in waste treatment, hydrogen production by supercritical water gasification of coal and supercritical hydr thermal synthesis, were discussed.

Keywords. Supercritical water; property; application.

1. Introduction
As the most commonly used green medium in nature, water has been widely used in chemical reactions. Supercritical water has unique physicochemical properties and has been used as a reaction medium and solvent in many fields. Supercritical water has the characteristics of wide source, low price, non-toxic and harmless, and easy to be separated from the product. Supercritical water as a new reaction medium and solvent has a broad application prospect. Therefore, the application and research of supercritical water are paid more and more attention.

Compared with water at normal temperature and normal pressure, supercritical water had large differences and also had some unique characteristics. In this paper, some basic physical properties of supercritical water, included density, viscosity, thermal conductivity, dielectric constant, ion product, hydrogen bond, diffusion coefficient and solubility, were introduced. Some applications of supercritical water oxidation technology in waste treatment, hydrogen production by supercritical water gasification of coal and supercritical hydr thermal synthesis, were discussed.

2. Supercritical Water (SCW)
Water is the most widely used and important solvent in nature. The critical point of water is 374.3 °C and 22.1 MPa. The physical properties of supercritical water are obviously different from normal water. In the supercritical state, the density of water is lower than that of normal water (about 1/3). Lower viscosity, smaller 1-2 orders of magnitude compared to normal water; the thermal conductivity decreased slightly.

The dielectric constant decreases [1, 2]; The ion product increased greatly, which was 10-100 times of normal water. Hydrogen bonds between water molecules were significantly weakened [3, 4].
diffusion coefficient is increased by about 2 orders of magnitude compared with normal temperature water.

3. Properties of Supercritical Water

3.1. Density
The density of supercritical water can be changed by changing the pressure and temperature. At the critical point, the density of supercritical water is 0.326 g/cm$^3$, and the density of supercritical water oxidation is 0.1 g/cm$^3$. The density of supercritical water decreases with the increase of temperature and decrease of pressure, so the density of water can be adjusted by changing temperature and pressure.

3.2. Viscosity
When water is in supercritical state, its viscosity is usually an order of magnitude smaller than that of liquid. The viscosity of supercritical water (450 °C, 270 MPa) is about 0.298×10$^{-2}$ pa·s [5], which makes supercritical water become a highly liquid substance. The density of supercritical water decreases with the increase of temperature and increases with the increase of pressure. The viscosity of supercritical water is very close to the air under normal conditions, and it becomes a highly liquid material, making the diffusion of solute molecules in supercritical water extremely easy.

3.3. Thermal Conductivity
In general, the thermal conductivity of liquid decreases with the rise of temperature. The thermal conductivity of water at normal temperature and pressure is 0.598 W/ (m·K), and when it is in the critical state, the thermal conductivity of water is about 0.418 W/ (m·K), which does not change much [6]. The thermal conductivity and dynamic viscosity have similar functional expressions, but the thermal conductivity has stronger divergence characteristics and lacks local minimum value.

3.4. Dielectric Constant
The change of dielectric constant is related to the change of hydrogen bond. Under normal conditions (25 °C, 0.101 MPa), the dielectric constant of water is 78.46 due to hydrogen bonding. It is much higher than the permittivity of organic matter, and the permittivity value is an important parameter in chemical reaction research. Uematsu and Franck obtained the permittivity value of water when the pressure is from 0.1~500 MPa and 0~550 °C, and obtained the variation trend of water permittivity with temperature and pressure. With the increase of temperature, the value of water dielectric constant decreases, pressure increases, the value of water dielectric constant increases, and the influence of temperature is more prominent. Uematsu and Franck proposed the following formula to describe the relationship between hydrogen bonds and temperature and water density [7].

$$\varepsilon = 1 + \frac{A_1}{T}\rho + \left(\frac{A_2}{T} + A_3 + A_4 T\right)\rho^2 + \left(\frac{A_5}{T} + A_6 + A_7 T^2\right)\rho^3 + \left(\frac{A_8}{T^2} + A_9 + A_{10}\right)\rho^4$$

In the equation, $T$-temperature; $\rho$-Water density; $A$-fitting parameters.
When the temperature is 300 °C and the density of water is 0.75 g/cm$^3$, the dielectric constant is 21. When the temperature is 500 °C and the density of water is 0.30 g/cm$^3$, the dielectric constant is 4.1. In normal water, the permittivity is 7.8 [8]. With the increase of density, the permittivity of water increases, and with the increase of temperature, the permittivity of water decreases. The change of permittivity of water causes the change of solubility of supercritical water.

3.5. Ion Product
The ionic product of water is related to the density and temperature, but the density has a great influence on it. The higher the density is, the larger the ionic product of water will be. The ionic product of water at normal temperature and pressure is $K_w = 1 \times 10^{-14}$. Near the supercritical point,
the density of water decreases rapidly due to the rise of temperature, leading to the decrease of the ionic product. Marshall and Frank fitted the relationship between ion product and temperature and density [9]:

$$\log K_w = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^2} + \left(\frac{E + F}{T} + \frac{G}{T^2}\right) \log \rho$$

In the equation, \(T\)-temperature; \(\rho\)-Water density; \(A\sim G\)-fitting parameters.

Different ionization degree of water directly leads to different \(H^+\) in water, which has a great influence on the reaction of supercritical water. Antal et al. [10] believed that when \(K_w \geq 10^{-14}\), it was helpful for ion reaction. When \(K_w \geq 10^{-14}\) is helpful for free radical reaction, so free radical reaction plays a dominant role in the supercritical fluid region with high temperature and low density.

### 3.6. Hydrogen Bond

Hydrogen bonds of water molecules are one of the important factors that make up many unique properties of water. As temperature and water density change, hydrogen bonds between water molecules weaken and decrease. For example, when the density is 0.1 g/cm\(^3\) at 412 °C, 10%-14% hydrogen bonds exist in the external environment, while when the temperature is 356 °C and the density is 0.5 g/cm\(^3\), 30%-45% hydrogen bonds exist [11].

### 3.7. Diffusion Coefficient

The decrease of water density, viscosity and hydrogen bond will lead to the significant increase of water diffusion coefficient with the increase of temperature. When the density decreases from 1 g/cm\(^3\) to 0.1 g/cm\(^3\), the diffusion coefficient will increase by more than 10 times. Therefore, in the supercritical state, the diffusion coefficient is consistent with the high-temperature theoretical gas in quantity [12].

### 3.8. Solubility

For normal water, they can dissolve most inorganic substances, but most organic substances and gases are very low solubility. Supercritical water shows almost opposite properties, almost insoluble to inorganic matter, but soluble to organic matter and gas. Supercritical water is a very useful reaction medium because of its unusual solubility in organic matter and gas [13].

### 4. Application of Supercritical Water

#### 4.1. Application of Supercritical Water Oxidation Technology in Refractory Organic Compounds

Because of having high processing efficiency, supercritical water oxidation reaction completely, fast and wide use range, process as an object closed, reactor has simple structure, small volume, generated by the product does not require subsequent processing, do not form secondary pollution, and the advantages of inorganic salt can be recycled, more and more be taken seriously in the treatment of hazardous wastes.

Because of supercritical water oxidation technology are generalized, can oxidation degradation of the vast majority of poisonous and harmful waste, so for supercritical water oxidation technology at home and abroad on the oxidation of many waste processing application is studied.

#### 4.2. Supercritical Water Gasification of Coal for Hydrogen Production

Coal gasification in supercritical water is a new hydrogen production technology developed in recent years. The main chemical reactions of coal supercritical water gasification to prepare hydrogen are as follows [14, 15]:

- Steam reforming: \(C + H_2O \rightarrow CO + H_2\)
- Water vapor conversion: \(CO + H_2O \rightarrow CO_2 + H_2\)
- Methanation: \(CO + 3H_2 \rightarrow CH_4 + H_2\)
Wang et al. [16] studied the catalytic effect of Ca(OH)$_2$ on low-quality coal by gasifying coal in supercritical water in autoclouge. Yan Qihui et al. [17] added CMC and NaOH to CWS to explore the performance of catalytic gasification of coal /CMC in critical water to produce hydrogen.

4.3. Supercritical Water Thermal Synthesis
Supercritical hydrothermal preparation of nanomaterials and the nature of the catalytic materials in supercritical water as reaction medium, change of phase behavior, diffusion rate and the solvation effect, the traditional solvent under the condition of heterogeneous reaction is a homogeneous reaction, thus increasing the diffusion coefficient, reduce the mass transfer and heat transfer resistance, so as to control the phase separation process, shorten the reaction time, the synthesis of metal oxide nanomaterials or catalytic materials. Otsu et al. [18] using a supercritical hydrothermal synthesis method, a MnO, Ag2O and PbO prepared nanoparticles.

5. Conclusion
The study of supercritical water has other applications. As in most geological areas below the earth's crust, supercritical water can participate in mineralization. Japan Kobe Steel Corporation uses "supercritical water" as a disinfectant for precious fruits and vegetables. In recent years, supercritical water has been used as a solvent and reaction medium for its unique properties, and has been researched and applied in many fields. At present, the research on the properties of supercritical water is still in the exploratory stage, and many issues are still unclear. In the future, it is necessary to continue to vigorously carry out research in this area, and supercritical water technology will surely have a faster and newer development in the future.

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