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REVIEW

Energy conversion of biomass with supercritical and subcritical water using large-scale plants

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Exploiting unused or waste biomass as an alternative fuel is currently receiving much attention because of the potential reductions in CO_2 emissions and the lower cost in comparison to expensive fossil fuels. If we are to use biomass domestically or industrially, we must be able to convert biomass to high-quality and easy-to-use liquid, gas, or solid fuels that have high-calorific values, low moisture and ash contents, uniform composition, and suitable for stored over long periods. In biomass treatment, hot and high-pressure water including supercritical and subcritical water is an excellent solvent, as it is clean and safe and its action on biomass can be optimized by varying the temperature and pressure. In this article, the conversion of waste biomass to fuel using hot and high-pressure water is reviewed, and the following examples are presented: the production of large amounts of hydrogen from waste biomass, the production of cheap bioethanol from non-food raw materials, and the production of composite powder fuel from refractory waste biomass in the rubble from the Great East Japan Earthquake. Several promising techniques for the conversion of biomass have been demonstrated in large-scale plants and commercial deployment is expected in the near future.

[**Key words:** Biomass; Supercritical water; Subcritical water; Superheated steam; Gasification; Bioethanol; Powder fuel; Energy utilization]

To reduce CO_2 emissions and move away from an oil-dependent society, it is imperative to develop alternative energy resources to fossil fuels. Recently, biomass has received much attention as a renewable energy source, and research on the conversion of biomass to high-performance and easy-to-use fuels or energy is being promoted in many countries. Japan produces 370 million tons of biomass per year and about 77 million tons (20%) of this are disposed of without being further utilized (1). The conversion of this waste biomass to bio-fuels or bio-chemicals could be effective in reducing CO_2 emissions and preserving fossil fuels. Biomass is a promising new energy resource but there are several difficulties associated with its use as a fuel: (i) its high moisture content and low calorific value per weight, (ii) large seasonal and areal variations in its composition, and (iii) long-term storage is difficult because it begins to rot quickly. As a result of these drawbacks, the possibility of direct combustion of crude biomass is limited in current incineration systems and energy production facilities, which require homogenous fuels with high-calorific value, low ash content, and low water content. Therefore, biomass processing to produce user-friendly and high-efficiency fuels is important, and this processing must be both environmentally friendly and economical.

New techniques using water at high temperature and high pressure, which is referred to as supercritical water, subcritical water, or high-pressure superheated steam, have been recently developed for biomass utilization (2–4). Typical applications of hot and high-pressure water to biomass are (i) the gasification and production of fuel gas such as hydrogen and methane; (ii) the production of liquid fuels such as bioethanol, biodiesel oil, and methanol; and (iii) the production of solid fuels such as charcoal and composite solid fuels with biomass or waste plastic. Compared to conventional techniques for producing fuel and energy from biomass, these new techniques using hot and high-pressure water can bypass the drying or dewatering process, reduce the reaction temperature, shorten the reaction time, suppress char production, and increase the product yield. There are, however, several disadvantages; for example, operating at high pressure is necessary and corrosion problems can occur. Further research into fully exploiting the advantages and minimizing the disadvantages of these techniques is very important.

There are many reviews of the applications of supercritical water, subcritical water, and high-pressure superheated steam. Biomass utilization using hot and high-pressure water is introduced in several books (5–7), and the properties and applications of supercritical and subcritical water are discussed in several references (8–10). In the following, the literature on each specific topic will be introduced in the corresponding section.

CHARACTERISTICS OF WATER IN THE HIGH-TEMPERATURE AND HIGH-PRESSURE REGION

Water, which is the most common and important solvent in nature, has many attractive characteristics as a reaction medium,

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extraction solvent, and salvation solvent; it is a harmless, cheap, and environmentally friendly solvent, and it is also a very polar solvent. The properties of water change significantly depending on the temperature and pressure, and its properties at high temperatures are very different to those under ambient conditions. Here, the conversion of biomass to fuel or energy using three kinds of water is considered: supercritical water, which is above the critical temperature (374°C) and critical pressure (22.1 MPa); subcritical water, which is below the critical temperature and above the vapor pressure at that temperature; and high-pressure superheated steam, which is above the critical temperature and below the critical pressure. The temperature and pressure regions in which each type of water exists are shown in the phase diagram of water in Fig. 1.

Variability of the density of water Fig. 2 shows the relationship between the temperature, pressure, and density of water (11). CP denotes the critical point of water and is located at the critical temperature of 374°C, critical pressure of 22.1 MPa, and critical density of 0.322 g/cm^3. Liquid water exists to the right-hand side of the CP above the convex curve, and to the left-hand side is steam. The density of liquid water at room temperature is 1 g/cm^3, as shown by point A, and that of steam is 0.000017 g/cm^3, as shown by point B. Both points mark an equilibrium relation and are connected by a horizontal dotted line (in this case, the dotted line is nearly on the *x*-axis). Subcritical water at 200–300°C and 1.6–8 MPa, shown by points C and D, can be used for treatment of biomass and has a density in the range 0.865–0.712 g/cm^3. The densities of liquid water and steam overlap with the CP. Supercritical water exists above the CP, and its density at 390°C and 25 MPa is 0.215 g/cm^3 (point E), and at 450°C and the same pressure, it is 0.109 g/cm^3 (point F). The density of water changes significantly in the high-temperature region and, as a result, its solvating power varies from low (steam) to high (liquid). The solvency power of supercritical and subcritical water is intermediate between steam and liquid water.

Variability of the dielectric constant of water The second important and highly variable property of water is the dielectric constant. Fig. 3 shows the dependence of the dielectric constant on temperature and pressure (12). This parameter is a measure

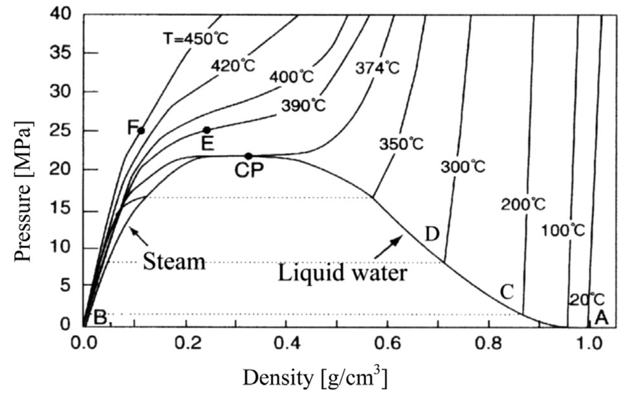

FIG. 2. Relationship between temperature, pressure, and density of water.

of the polarity of a solvent; a solvent with a large value can dissolve polar and ionic materials such as acids, alkalis, and salts, and a solvent with a small value shows the opposite tendency. The dielectric constant of liquid water at room temperature and atmospheric pressure is about 80, which is one of the highest values of many solvents. Water at room temperature can dissolve polar compounds but cannot dissolve non-polar compounds such as oil or many kinds of organic compounds. However, the value of subcritical water at 200°C and 1.6 MPa (saturated vapor pressure) is about 35 and that of supercritical water at 400°C and 25 MPa is 2.5, which is close to that of benzene at room temperature. As a result, in the high-temperature region, water becomes subcritical or supercritical water and the solubility of non-polar organic compounds increases, but that of polar compounds decreases.

Variability of the ionic product of water The third important and highly variable property is the ionic product (K_W). This

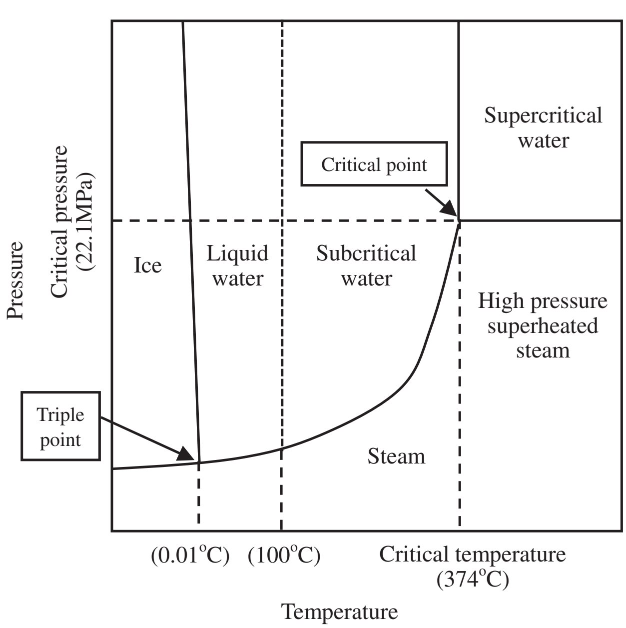

FIG. 1. Phase diagram of water.

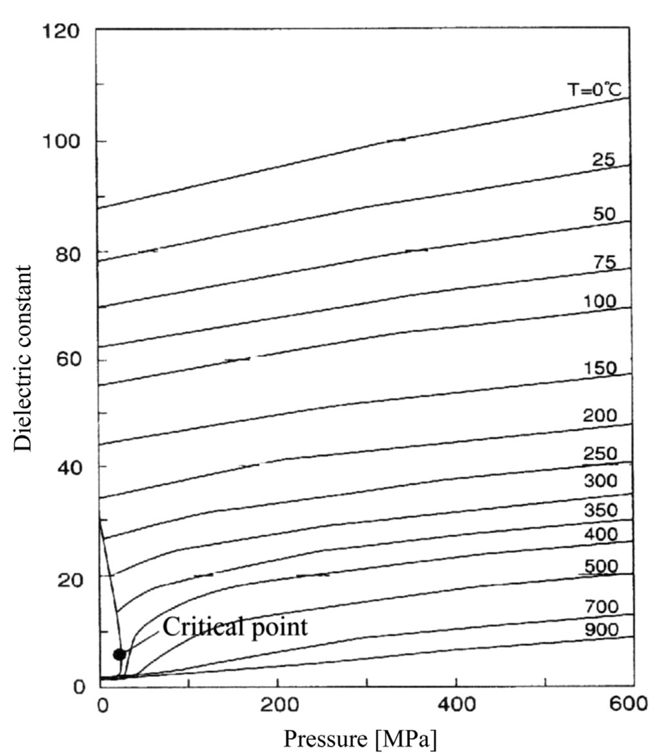

FIG. 3. Dependence of dielectric constant of water on temperature and pressure.