Research Activity on Supercritical Fluids Technology at Kumamoto University

Biomass Treatment with Sub- and Supercritical Water

Water at sub- and supercritical conditions is considered a promising solvent for degradation of hazardous waste into harmless compounds. By varying the density (a strong function of pressure and temperature), it is possible to change the other properties of water, such as the dielectric constant and ion product. The density of water is an important property in determining reaction mechanisms at supercritical water conditions. Supercritical water not only participates in a reaction as a solvent but also as a reactant. At sub- and supercritical water conditions, there are two major reactions: oxidation and hydrolysis. In supercritical water, organic materials are completely converted into carbon dioxide, water and nitrogen. Another important reaction is the conversion of organic materials into useful chemical compounds.

Biomass is a term used to describe all the organic materials derived from living matter and it represents a renewable and alternative source for the production of chemicals. Biomass is also potentially one of the most promising alternatives for electrical power production owing to its ecological advantages. The development of process has been proposed to recover chemical resources from biomass waste and zero emission processes that can accomplish the destruction of the wastes into harmless compounds, such as hydrogen, carbon dioxide and methane. Plant biomass approximately consists of 40–45 wt%of cellulose, 25–35 wt% of hemicellulose, 15–30 wt% of lignin and up to 10 wt% other compounds.

We have reported decomposition of biomass wastes at sub- and supercritical water in batch and flow reactor. Lignin, which is the second most abundant polymeric aromatic organic substance in wood biomass after cellulose, and contains many oxygen-based functional groups, has been investigated as an alternative source of chemical compounds. Guaiacol, as model compound of lignin, has been decomposed to produce other chemical compounds [33]. Lignin has also been decomposed to recover phenolic compounds, such as cathecol, phenol and cresol [34].

Tar, a part of biomass waste, has high impact on the environment and on humans but it also contains many chemical compounds that can be used for industrial applications. This hazardous waste, however, has been discarded without any treatment because there is currently no method with which tar can be converted to fuels and chemical intermediates easily in an environmentally friendly way. Recovery of phenol through decomposition of tar at hydrothermal alkaline condition and liquefaction kinetic of tar in sub- and supercritical water has been studied [35-37].

Glucose as a part of cellulose, in particular, can be converted into energy using diverse methods. For example, in a conventional reaction method, it can be converted into low-molecular-weight saccharides as decomposition products. However, the acid catalysts such as sulfuric or hydrochloric acids were used in this process. And, the process was to be complicate because removal of the harmful catalyst that remains after the process is required. Therefore, the development of new environmentally friendly synthetic methods with high economic efficiency is desired. In our laboratory, the decomposition of glucose has been carried out under various experimental conditions in subcritical water using continuous-flow reactors. The decomposition products, such as fructose, glyceraldehydes, glycolaldehyde, 5-HMF, and 2-furfural were obtained [38].

In addition, study of decomposition of biomass model compounds was conducted

at hydrothermal electrolysis in batch and flow reactors as shown in Figure 3 (a) and (b), respectively. In this work, we focused on understanding the degradation behavior of glucose under hydrothermal conditions and to determine how to obtain gaseous compounds such as hydrogen and carbon dioxide. Electrode oxidation reaction of glucose at 250 °C was conducted to investigate fundamental reaction characteristics for the purpose of utilizing glucose solution [39]. Other compounds, such 1-butanol and glycerol were also used as starting materials to produce hydrogen as alternative energy.

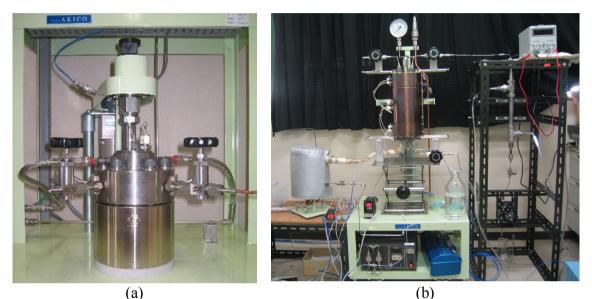


Figure 3. Hydrothermal electrolysis apparatus. (a) autoclave (batch type); (b) flow type.

References

- [33] Wahyudiono, T. Kanetake, M. Sasaki, M. Goto, *Chem. Eng. Technol.*, Vol. 30, 2007, p. 1113.
- [34] Wahyudiono, M. Sasaki, M. Goto, Chem. Eng. Process., Vol. 47, 2008, p. 1609.
- [35] Wahyudiono, S. Fujinaga, M. Sasaki, M. Goto, *Chem. Eng. Technol.*, Vol. 29, 2006, p. 882.
- [36] Wahyudiono, M. Sasaki, M. Goto, J. Mater. Cycles Waste Manage., Vol., 2007, p.
- [37] Wahyudiono, M. Sasaki, M. Goto, Polym. Degrad. Stab., Vol. 93, 2008, p. 1194.
- [38] Saito, T., Sasaki, M., Kawanabe, H., Yoshino, Y., Goto, M., *Chem. Eng. Technol.*, Vol. 32, **2009**, p. 1.
- [39] M. Sasaki, K. Yamamoto, M. Goto, J. Mater. Cycles Waste Manag., Vol. 9, 2007, p. 40.