Useful Products from Lignocellulosics by Supercritical Water Technologies

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Abstract: Supercritical fluid technology has been applied to convert lignocellulosics into bioenergy and chemicals. As a result, it was found that lignocellulosics could be separated into carbohydrate-derived and lignin-derived products by supercritical water treatment. A detailed study of these products revealed that useful products such as oligosaccharides and related substances could be achieved for subsequent ethanol fermentation. It was further found that the prolonged treatment could produce various organic acids for subsequent methanogen to produce methane and methanol. Based on these lines of research achievements, supercritical water technologies were proved to be powerful to produce useful bioproducts from lignocellulosics.

Keywords: Lignocellulosics, Supercritical Water, Ethanol, Organic Acid, Lignin-derived Products

1. INTRODUCTION

Due to global warming caused by excessive use of fossil resources, renewable biomass resources will become more important in the future as alternatives to fossil fuels. Various conversion technologies of biomass resources have, therefore, been investigated. Bobleter proposed hydrothermal treatment of lignocellulosics without using any catalyst, and reported its excellent conversion [1]. In our research, not only subcritical (hydrothermal) but also supercritical fluid technologies have been applied to lignocellulosics to obtain bioenergy and useful chemicals [2-12]. As a result, we have reported that lignocellulosics can be separated to carbohydrate-derived and lignin-derived products by supercritical water treatment (>374°C / >22.1MPa) [2]. The former products, which mainly consist of polysaccharides, oligosaccharides, and their decomposed products, have a potential as a substrate for ethanol fermentation [6, 11, 12], while the lignin-derived products, which mainly consist of monomeric and oligomeric materials, may be useful substitutes for the chemicals from fossil resources [12]. In this paper, therefore, we will introduce supercritical water technologies and their applications to various fuels and chemicals.

2. EXPERIMENTAL

The batch-type and flow-type supercritical water biomass conversion systems used in this study are shown in Fig. 1. These systems can cover a range up to 280MPa and 500°C in the former, and up to 45MPa and 450°C in the latter [6].

For the batch-type system, distilled water was fed with samples to the 5ml reaction vessel made of Inconel-625. Subsequently, it was heated by immersing it into the molten tin bath, and the reaction vessel was immersed into the water bath to quench. During this treatment, the temperature and pressure in the reaction vessel were monitored by thermocouple and pressure gauge attached to the reaction vessel, respectively.

The flow-type system shown in Fig. 1 can be divided into a slurried sample of water was routinely stirred by the circulating pump to keep its concentration constant, which prevented the sample from precipitating. The sample was injected into the reaction tube of length 19mm, and pressurized by the slurry injector up to an appropriate pressure. The sample was then mixed with the supercritical water prepared by the solvent pumping section. After the reactant passed through the reaction tube, an appropriate amount of the water was injected into the reaction vessel to quench the reaction and its mixture was further cooled by passing through the cooler.

Fig. 2 shows the fractionation scheme of the sample treated in supercritical water. The treated sample was filtrated into the supercritical (SC) water-soluble and SC water-insoluble portions. During the setting for 12h, the former was precipitated due to the change of dielectric constant of water from the supercritical state to the ordinary one, and precipitates (water-insoluble) were filtrated to separate from the solution. In addition, precipitates were washed by methanol, and separated into precipitates and methanol-

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soluble portion. SC-water-insoluble portion were also washed with methanol and separated into methanol-soluble portion and methanol-insoluble residue.

3. SUPERCRITICAL WATER TECHNOLOGIES

3.1 Decomposition behavior

From the present investigations, we propose a pathway of cellulose decomposition by hydrolysis, dehydration and fragmentation [6]. In the first place, cellulose is hydrolyzed to polysaccharides and oligosaccharides. The DP in the former is in range between 13 and 100, while that in the latter is between 2 and 12, whose reducing end of glucose is dehydrated and fragmented to levoglucosan, erythrose and glycolaldehyde. These dehydrated and fragmented oligosaccharides are, further, hydrolyzed in the oligosaccharide portion to glucose, which is isomerized to fructose. The resultant hexoses are then further decomposed, if the treatment is prolonged, to levoglucosan, 5-hydroxymethyl furfural, erythrose, glycolaldehyde, methylglyoxal, and dihydroxyacetone by way of dehydration and fragmentation.

Considering that the hexoses are the best for alcohol fermentation, a comparison of the yield of hexose is necessary between the batch-type and flow-type systems. It is known that the higher treatment pressure for supercritical water gives a higher density and concomitantly a higher ionic product of water; densities and ionic products of supercritical water (380°C, 40 and 380°C, 100MPa) were 0.60 and 0.72g/cm³ in density, and 10.0-12.1 and 10.0-10.8 mol²/l² in the ionic product, respectively. These results, therefore, suggest that the higher treatment pressure is better for hydrolysis reaction due to the enhanced effect of hydrolyzing ability. Although the flow-type system provided the higher yield of hydrolysates, compared with the batch-type system, the yield of glucose in the flow-type system was lower than that in the batch-type system. This dilemma is due to the limitation of the pressure regulator of the flow–type system only up to 45MPa.

Lignocellulosics were treated in supercritical water (>374°C, >22.1MPa), and fractionated into water-soluble portion, precipitates, methanol-soluble portion and methanol-insoluble residue. The water-soluble portion contained carbohydrate-derived hydrolyzed products, dehydrated products, fragmented products and organic acids. The precipitates were found to be glucan which is insoluble in ordinary water but soluble in supercritical water. Methanol-soluble portion was found to be derived from lignin. Based on these results, the supercritical water treatment was concluded to be appropriate to use as a pretreatment for ethanol fermentation, methane fermentation and hydrogen production.

Fig. 2 Fractionation of the sample treated in supercritical water [6].

Fig. 3 Decomposition behavior of cellulose in supercritical water [6]
3.2 Lignin-derived products

Japanese cedar (*Cryptomeria japonica* D. Don) wood was treated with supercritical water (>374°C, >22.1 MPa), and fractionated into the water-soluble portion, the methanol-soluble portion, and the methanol-insoluble residue. The methanol-soluble portion mainly consisted of the lignin-derived products [8,9,10]. To characterize the compounds in the methanol-soluble portion, gel permeation chromatographic (GPC) and gas chromatographic-mass spectrometric (GC-MS) analyses were performed [9, 10]. The GPC analysis indicated that the methanol-soluble portion contained lignin-derived monomeric and dimeric products. GC-MS analysis detected 31 products which were expected to be monomeric compounds, and 18 of these were identified to be guaiacol, methylguaiacol, ethylguaiacol, vinylguaiacol, eugenol, propylguaiacol, vanillin, *cis*-isoeugenol, *trans*-isoeugenol, acetoguaiaconone, propioguaiaconone, guaiacylacetaone, 2-methoxy-4-(1-hydroxypropyl)phenol, homo-vanillic acid, 2-methoxy-4-(prop-1-en-3-one)phenol, coniferyl aldehyde, and ferulic acid. In addition, 22 dimeric products were detected, and 4 of these were believed to be compounds with biphenyl type (5-5), diphenylethane type (β-1), stilbene type (β-1), and phenylcoumaran type (β-5) structures. These results clearly indicated that the methanol-soluble portion included various monomeric and dimeric compounds produced as a result of the cleavage of ether linkages and propyl chains of lignin. These lignin-derived products have a possibility of utilizing as alternative chemicals of fossil resources in the future.

![Fig. 4](image)

**Fig. 4** Total ion chromatography of methanol-soluble portions from Japanese cedar wood by supercritical water treatment (380°C, 100 MPa, 7 sec) [9]

3.3 Ethanol production process using supercritical water technology

As a result of decomposition behavior of cellulose, it can be simulated that the saccharides produced from lignocellulosics by supercritical water treatment are converted to ethanol through fermentation (Fig. 5). In its ethanol production process, lignocellulosics are converted into 2 parts, water-soluble portion with precipitates and methanol-soluble portion. The former is converted into monosaccharides by enzymatic saccharification or dilute acid hydrolysis, followed by fermentation to ethanol. On the other hand, The latter, methanol-soluble portion, is collected as lignin-derived products [6,7].

![Fig. 5](image)

**Fig. 5** Scheme of ethanol production from lignocellulosics using supercritical water technology [7]
3.4 Methane and bio-hydrogen production process from lignocellulosics

Fig. 6 shows production process of methane, methanol and hydrogen from lignocellulosics. Lignocellulosics can be decomposed in supercritical water (>374°C, >22.1MPa) and converted to various useful products, such as polysaccharides, oligosaccharides and monosaccharides, as discussed in a previous section. However, the treatment time is prolonged, these substrates are further decomposed into organic acids, namely, formic acid, glycolic acid, acetic acid pyruvic acid and lactic acid. The obtained these organic acids are appropriate substrates of methane production in anaerobic fermentation [11]. Thus, they can be converted into methane. This process by supercritical water treatment to produce organic acids from lignocellulosics is so short, compared with that by acid production bacteria in nature.

It was reported that the organic acids could be produced from Japanese beech (*Fagus crenata*) in supercritical water. During a relatively short supercritical water treatment (5sec, 380°C, 100MPa), cellulose and hemicellulose were decomposed to formic, pyruvic, glycolic, acetic and lactic acids, but there was little in production of organic acids from lignin under these conditions. However, during more prolonged treatment (4min, 380°C, 100MPa), propyl side-chains of phenylpropane unit of lignin were found to be decomposed to organic acids.

Additional study in this project is on a selective production of formic acid from lignocellulosics by hot-compressed and supercritical water treatments. Formic acid is known to be a good substrate to produce hydrogen by *Escherichia coli* genetically engineered with formate hydrogenlyase. The hydrogenlyase activity can be catalyzed by formic dehydrogenase and hydrogenase functioning together in a coupled electron transfer system. However, its yield is lower than other organic acids in supercritical water because of its ease in decomposition. Through our extensive studies, however, we could find a treatment condition to have a higher yield of formic acid with lower yield of other organic acids as treated by subcritical water with hydrogen peroxide (H₂O₂) [13].

Through these lines of study, methane, methanol and hydrogen were found to be achieved from lignocellulosics by supercritical water treatment, which can cultivate a new renewable bioenergy in sustainable energy systems.

![Fig. 6 Production process of methane, methanol and bio-hydrogen from lignocellulosics [11]](image)

4. CONCLUSION

By using supercritical or subcritical water treatment, lignocellulosics can be decomposed and separated into water-soluble portion, precipitates, methanol-soluble portion and water-insoluble residue. The water-soluble portion and precipitates contained mainly products derived from carbohydrates (cellulose and hemicellulose), which is appropriate for producing ethanol. On the other hand, lignin-derived products were mainly obtained in methanol-soluble portion. These products have a possibility of utilizing as alternative chemicals of fossil resources. If the treatment is prolonged, organic acids were found to be produced in water-soluble portion, which are available for producing methane and hydrogen. Through these lines of study, it was found that lignocellulosics could be converted to useful bioenergies such as ethanol, methane, methanol and bio-hydrogen for establishing sustainable energy systems.

5. REFERENCES


