



Preliminary Investigation on the Useful Chemicals obtained from High-Temperature and High-Pressure Water Treatment of Hinoki (*Chamaecyparis Obutus*) Bark

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Abstract

The possibility of utilizing residual forest biomass to produce valuable chemicals was investigated. An outer layer of a bark of Hinoki (*Chamaecyparis obtusa*) tree, a Japanese cypress, was used as a sample material. Experiments were carried out in a semibatch reactor apparatus that allows the study of the effect of reaction temperatures in a single run. Analysis of the products by GC-MS reveals formation of useful compounds such as furfural, some aromatic compounds (1,3-di-*tert*-butyl benzene and 2,4-di-*tert*-butyl phenol), and fatty acids (myristic acid, palmitic acid and stearic acid).

Keywords: fatty acids, furfural, high temperature water treatment, hinoki, residual biomass

1. Introduction

Over-dependence of the chemical industry on non-renewable fossil fuels such as crude oil or natural gas may lead to further increase in global warming. This is detrimental to the environment, and could put lives on earth at stake if not given proper consideration. In order to lessen the dependency of industry on non-renewable materials, in line with the Kyoto Protocol of 1997 on climate change to reduce CO₂ emission to the atmosphere, utilization of agricultural and forest residues is being considered for production of useful chemicals. Applicable treatment technologies are sought, one of these is the use of high-temperature and high-pressure (HTHP) water.

The application of HTHP water to recover useful materials from various organic wastes, with the general purpose of mitigating environmental pollution, has been attracting attention of many researchers and environmentalists. As a recognized environmentally benign solvent, the use of water offers ecological benefits for clean industrial processes. Chemical reactions in sub-and supercritical water media have attracted considerable interests (Faisal *et al.*, 2007a; Faisal *et al.*, 2008). To date, numerous articles have been written on the application to chemical synthesis and decomposition as have been reported by Savage (1999). Moreover, the use of sub and supercritical water is an emerging technique that can provide com-

plete decomposition of organic (Goto *et al.*, 1999) and hazardous wastes such as PCB and dioxins ((Staszak *et al.*, 1987; Yamasaki *et al.*, 1980; Anitescu and Tavlarides, 2000). This has also been applied as a medium for recovery of useful materials from various organic wastes such as plastics (Faisal *et al.*, 2007b), cellulose (Sasaki *et al.*, 1998), lignin (Saka and Konishi, 2000) and proteins (Faisal *et al.*, 2005; Kang *et al.*, 2001a; Daimon *et al.*, 2001).

Utilization of residual biomass to produce value-added chemicals by reaction in an environmentally benign and cheap solvent (*i.e.* HTHP water) is ecologically and industrially promising. This is investigated in this study taking an outer layer of a bark of Hinoki (*Chamaecyparis obtusa*), a Japanese cypress, as a test material. Unlike the conventional steam distillation or the emerging supercritical fluid extraction method, it is likely that chemical reaction or decomposition also take place using this method.

2. Methodology

Experiments were carried out in a semibatch reactor apparatus (B-100S, Organo Corporation) shown in Figure 1. This apparatus, capable of investigating the effect of increasing reaction temperatures in a single run, has been described in details elsewhere (Kang *et al.*, 2001b). This consists of a feed tank,

pump, preheater, reactor, cooling unit, regulator valve and sample collection vessel. De-ionized water is delivered by high-pressure pump (NP-CX-40, NSK Corp.) at required constant flow rate.

The water passes through the preheater before entering the reactor vessel. The 100-cm³ reactor and other connecting elements are made of Inconel 625 (Ni, Cr, Mo and Fe alloy). This can be operated at a maximum temperature of 500°C and a maximum pressure of 40 MPa. A 60- μ m filter is placed before the inlet pump and pressure regulator.

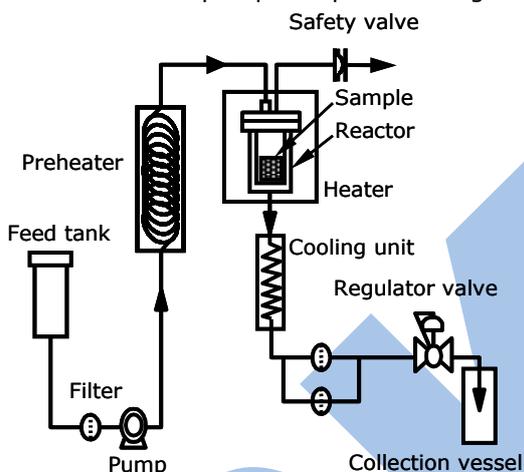


Figure 1. Schematic diagram of semi-batch reactor apparatus.

The outer layer of a bark of *Hinoki* was cut into small pieces of about 5 mm wide, having a thickness of about 1 mm. A 5.3 g sample was placed in the reactor. The water was allowed to flow through the reactor, then, the temperature was set to 450°C. Sample was collected continuously while the temperature increased, changing the sampling container after each sampling period. Extraction of the products from the mixture was performed using diethyl ether prior to each analytical run.

Analyses of the products were performed using a GC-MS apparatus (Hewlett-Packard, HP5973), equipped with HP-5MS column (Hewlett-Packard, 30 m x 0.25 mm x 0.25 μ m). Sample of about 2 μ l was injected to a sampling port set at 300°C, the split ratio was 100:1.

The temperature-programmed run was 35°C for 10 min, and increasing gradually to 300°C at a rate of 10°C/min. Helium was used as a carrier gas. The total organic carbon (TOC) and dissolved organic carbon (DOC) were measured using a TOC-500 analyzer.

3. Results and Discussion

A typical GC-MS chromatogram of liquid effluent obtained at 350 °C is shown in Figure 2. The major products identified consist of furfural, aromatic compounds (1,3-di-*tert*-butyl benzene, 2,4-di-*tert*-butyl phenol), and fatty acids such as myristic acid (tetradecanoic acid), palmitic acid (hexadecanoic acid) and stearic acid (octadecanoic acid). These compounds are mainly used as resins and antioxidants, as raw materials for the synthesis of other useful compounds, in cosmetic industries, among others. The chemical structures and major uses of each compound are summarized in Table 1.

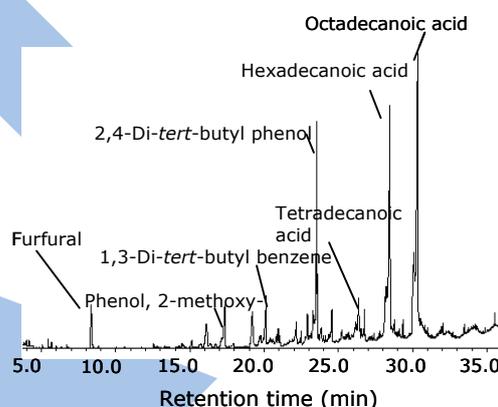


Figure 2. GC-MS chromatogram of liquid effluent obtained at 300°C (Diethyl ether was used as the extractant).

The effect of reaction temperature on the amount of various compounds produced, expressed in terms of area of each peak, is shown in Figure 2 and 3. The maximum peak area for almost all compounds was obtained at 350°C, except for furfural having a maximum peak at 320°C. It is possible that decomposition of these products took place at temperatures higher than the abovementioned temperatures.

Figure 4 shows the TOC, DOC and POC profile with time, along with the reaction temperature profile. There is an abrupt increase in TOC between 250 – 350°C, the temperature where the ion product of water is maximum. Based on the TOC profile, it is most likely that reaction occurred around this temperature.

3.1 Speculated Mechanism of Product Formation

Wood samples have been reported to contain about 40 – 50% cellulose, 5 – 20% hemicellulose and 20 – 30 % lignin. The products have been derived from these components

Table 1. Chemical structures of the compounds identified in liquid effluent and their uses.

| Products | Structures | Uses |
|---|--|---|
| Furfural *CAS [98-01-1] | | Solvent, Material of furan resin and THF, Medicines, Aromatics, etc. |
| 1,3-Di- <i>tert</i> -butyl benzene CAS [1014-60-4] | | — |
| 2,4-Di- <i>tert</i> -butyl phenol CAS [96-76-4] | | Antioxidant, Resin additives, Material for organic synthesis, etc. |
| Tetradecanoic acid (Myristic acid) CAS [544-63-8] | $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ | Material of esters, Cosmetics, Surfactant, Soap, etc. |
| Hexadecanoic acid (Palmitic acid) CAS [57-10-3] | $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ | Material of esters, Cosmetics, Surfactant, Soap, etc. |
| Octadecanoic acid (Stearic acid) CAS [57-11-4] | $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ | Industrial rubber, Crayon, Plasticizer, Cosmetics, Surfactant, Soap, etc. |

*CAS = CAS (Chemical Abstracts Service) registry number.

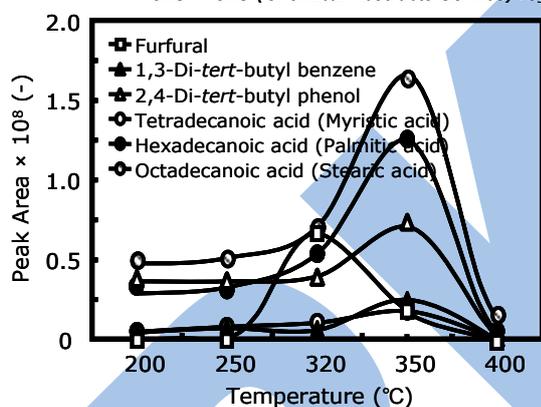


Figure 3. Effect of reaction temperature on the yield of each product based on the peak area of chromatograms.

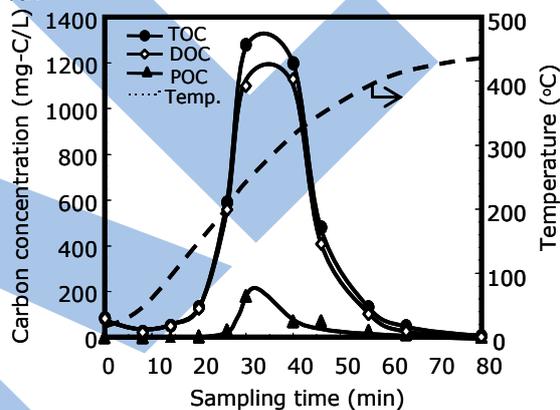


Figure 4. Carbon concentration and reaction temperature profile with time.

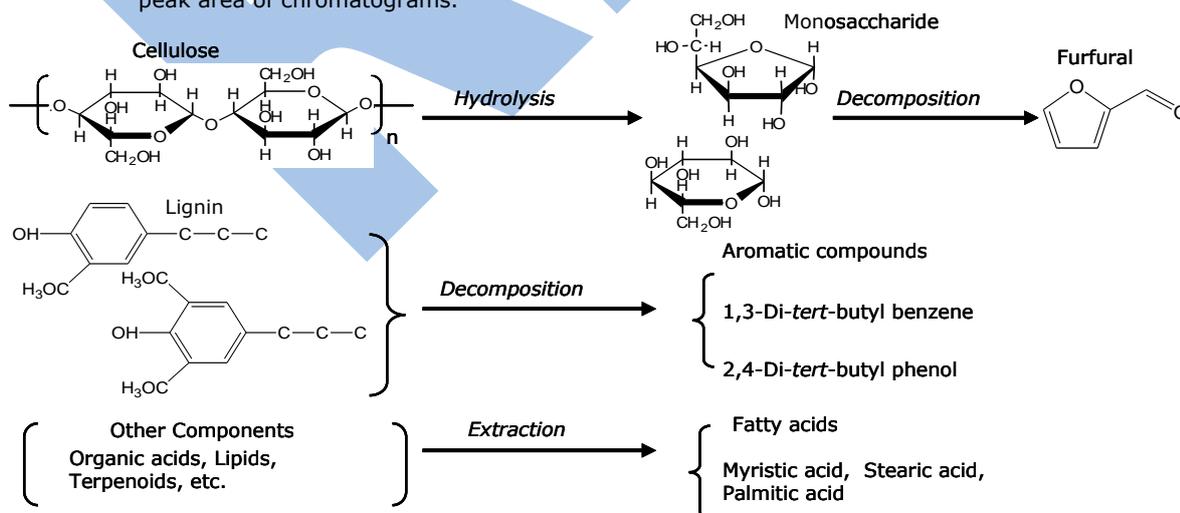


Figure 5. Speculated general mechanism of product formation.

in wood samples, and the speculated general mechanism of product formation is shown in Figure 5. Furfural is most likely derived from

further decomposition of glucose, a product of hydrolysis of cellulose. This was also observed in the study of glucose

decomposition to various useful chemicals (Holgate *et al.*, 1995). On the other hand, lignin could have been decomposed to form aromatic compounds such as those identified by GC-MS – namely, 1,3-di-*tert*-butyl benzene and 2,4-di-*tert*-butyl phenol. Extraction of fatty acids such as myristic acid, stearic acid and palmitic acid could have also taken place.

Based on the results, unlike the typical methods of treatment by steam distillation or supercritical fluid extraction, several products could be obtained from the near-critical water treatment of Hinoki.

3. Conclusion

This research shows the possibility of obtaining valuable chemicals from residual forest biomass represented by the bark of *Hinoki*, a Japanese cypress. Various chemicals were identified by GC-MS analysis, including furfural, some aromatic compounds (1,3-di-*tert*-butyl benzene and 2,4-di-*tert*-butyl phenol), and fatty acids (such as myristic acid, palmitic acid and stearic acid). This preliminary investigation might lay the groundwork for further studies on the effect of various parameters on the yield of each compound and elucidation of reaction mechanism and behavior of product formation under sub and supercritical conditions.

Acknowledgement

The research is funded by Japan Society for the Promotion of Science Research for the Future Program Project 97100504 (Causes and Effects of Environmental Loading and Its Reduction).

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