Available online at www.sciencedirect.com

ScienceDirect

Bioresource Technology 99 (2008) 1846–1852

BIORESOURCE TECHNOLOGY

Disassembly of lignin and chemical recovery in supercritical water and *p*-cresol mixture

Studies on lignin model compounds

Kazuhide Okuda, Satoshi Ohara, Mitsuo Umetsu, Seiichi Takami, Tadafumi Adschiri *

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

Received 25 June 2004; received in revised form 20 March 2007; accepted 20 March 2007
Available online 30 May 2007

Abstract

The aim of the study was to gain insight into the role of the each unit of lignin in the formation of products. Glycerol, guaiacol, the mixture of glycerol and guaiacol (Gly&Gua), and guaiacylglycerol-β-guaiacyl ether (GGGE) were used as lignin model compounds to study fragmentation of lignin in an excess of water and *p*-cresol at 400 °C. The products have been analyzed employing gas chromatography (GC)–mass spectrometer (MS) and gas chromatography-frame ionization detector for qualitative and quantitative analysis. GC–MS analysis indicated that phenol, *o*-cresol, methyl-anisole, di-methyl-phenol, ethyl-methyl-phenol, 2-(hydroxy-benzyl)-4-methyl-phenol (BMP) and 2-(2-hydroxy-5-methyl-benzyl)-4-methyl-phenol were formed. The products were similar to the products by the fragmentation of lignin. The products, except *o*-cresol, were primarily derived from glycerol and/or guaiacol. We also found that the amount of BMP derived from GGGE, which has glycerol unit and guaiacol unit in its structure, is much more than that derived from Gly&Gua. The increase of the BMP yield by reaction with GGGE compared with (glycerol and/or guaiacol) indicates that guaiacylglycerol unit with linkage of Gly&Gua plays an important role in the formation of BMP and also it is suggested that the BMP formation from GGGE has pathways other than that from Gly&Gua.

Keywords: Lignin model compounds; Supercritical water and *p*-cresol mixture; GC–MS (FID); Chemical recovery; Formation pathway

1. Introduction

Plant biomass has attracted resent interest as a potential substitute for petroleum. Various conversion processes are proposed that liquefy biomass to use as the alternative source of fuel (Mok and Antal, 1992; Ando et al., 2000; Sakaki et al., 1996; Antal et al., 2000; Sasaki et al., 1998, 2000). In addition to the use as a fuel, biomass is also a rich source of chemicals (Dorrestijn et al., 2000). Plant biomass consists of approximately 50 wt% cellulose, 30 wt% hemicellulose, and 20 wt% lignin. Lignin is a complex heteropolymer of trans-*p*-coumaryl, coniferyl, and sinapyl alcohols (Lin and Dence, 1992; Adler, 1977; Nakano, 1992) and is a potential source of aromatic chemicals. Freudenberg (1939); reported the production of vanillin from lignin by an alkali-nitrobenzene method (Nakano, 1992). One of the authors (Saisu et al., 2003) also demonstrated the conversion of organosolv lignin, which is a soluble component of lignin in organic solvents, into chemicals in a water–phenol (2.5:0.75 g) mixture at 400 °C. However, prolonged reaction time can result in uncontrolled polymerization during the decomposition process, leading to low conversion/selectivity and the formation of char. We found that an increase in the ratio of phenol, which presumably serves as a capping agent for reactive intermediate products to prevent unfavorable polymerization, decreased the formation of char (Okuda et al., 2004a,b). Recently, we have succeeded in the complete dissolution of lignin in a water-*p*-cresol (1.8:2.5 g) mixture at 400 °C without formation of char. We also successfully converted lignin into chemicals with low molecular weight

---

* Corresponding author. Tel.: +81 222175629; fax: +81 222175631.
E-mail address: ajiri@tagen.tohoku.ac.jp (T. Adschiri).

0960-8524/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2007.03.062

selectively under the same conditions (Okuda et al., 2004a,b). However, the origins of each product have not yet been reported in detail. In this study, the origins of each product were investigated by using model compounds of lignin, that is, glycerol, guaiacol, and guaiacylglycerol-β-guaiacyl ether (monomer unit of lignin with linkage of glycerol and guaiacol) in a water-*p*-cresol (1.8:2.5 g) mixture at 400 °C. The aim of the study is to gain insight into the role of the each unit of lignin in the formation of products.

2. Experimental

2.1. Materials

Glycerol and guaiacol (Fig. 1) were purchased from Wako Pure Chemical Industries (Japan) and guaiacylglycerol-β-guaiacyl ether (GGGE) was purchased from Tokyo Kasei Kogyo Co. Ltd. (Japan). Tetrahydrofuran (THF, HPLC grade) and *p*-cresol (99.0%) were purchased from Wako Pure Chemical Industries (Sendai, Japan) and were used without further purification.

2.2. Decomposition of lignin model compounds

All experiments were conducted using pressure-resistant vessels (SUS316, Akico Corporation (Tokyo, Japan)) whose inner volume was 5 mL. The vessel was loaded with one of the lignin model compounds, namely glycerol (0.1 g, 1 mmol), guaiacol (0.14 g, 1 mmol), glycerol and guaiacol (0.1 g + 0.14 g), and GGGE (0.1 g, 0.3 mmol). The vessel was also loaded with either distilled water (2.5 g) or a mixture of distilled water (1.8 g) and *p*-cresol (2.5 g) without purge by an inert gas. The vessel was then heated in an electric furnace (Akico Corporation (Tokyo, Japan)) whose internal surface temperature was maintained at 400 °C. The vessel was heated from room temperature to 400 °C within four minutes and the vessel was maintained at the same temperature as the furnace to within 1 °C. Reaction time in this study included the heat-up period. The pressure inside the vessel has not been measured. The reaction was conducted for approximately 0.25 to 3 h and ended by quenching the vessel in a water bath at room temperature. The reaction products were collected by rinsing the vessel with 50 mL of THF and separated into THF soluble and THF insoluble products using a 1.6 μm glass–fiber membrane filter. The products were completely soluble in THF and the THF insoluble products were negligible.

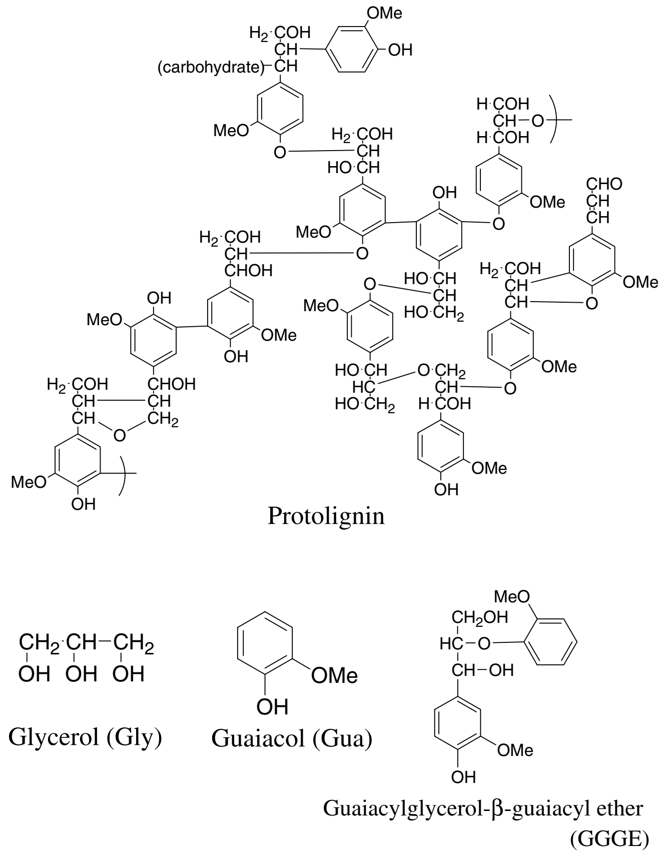

Fig. 1. Structural model of protolignin and structures of lignin model compounds.

2.3. Analytical methods

The THF soluble products (filtrates) were analyzed by a combination of gas chromatography (GC) and mass spectroscopy (MS) (GC–MS Saturn 2000, Varian (USA)) with

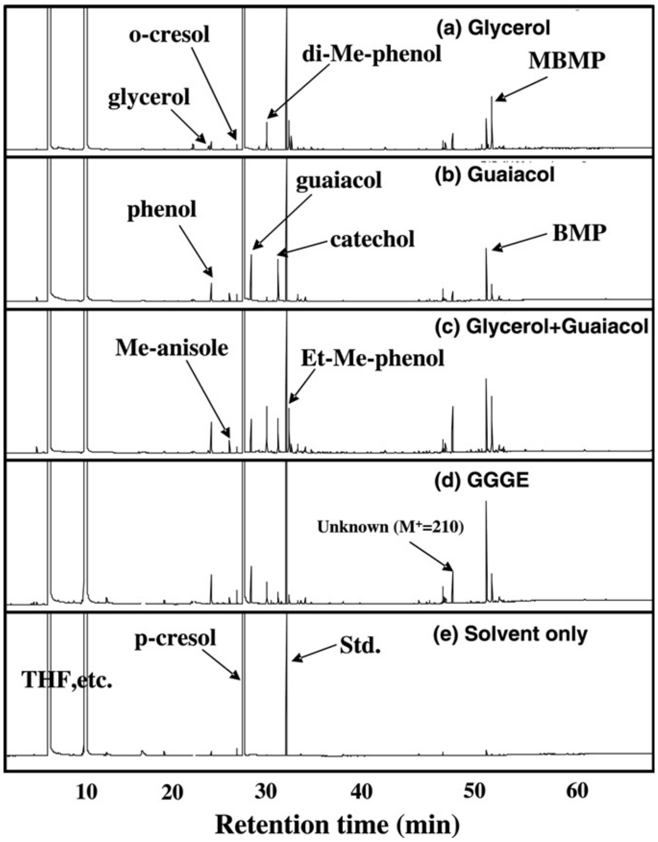

Fig. 2. The GC–FID chromatogram of the THF soluble products by the reaction with lignin model compounds in a mixture of water (1.8 g) and *p*-cresol (2.5 g) for 0.5 h at 673 K.