

Reactivity of lignin in pyrolysis studied by a series of dimeric lignin model compounds

H. Kawamoto, S. Horigoshi, S. Saka*

Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Tel/Fax: +81-75-753-4738; E-mail: saka@energy.kyoto-u.ac.jp

Reactivity of substructure in lignin in pyrolysis was evaluated at 400°C focusing on depolymerization, polymerization, carbonization, and gasification reactions by using a series of dimeric lignin model compounds.

Introduction

Thermochemical conversion of woody biomass is a possible method for transforming solid biomass into gas and liquid fuels and chemicals. However, selectivity in the products is usually low. In our laboratory, reaction mechanism of the component of woody biomass has been studied on molecular grounds in order to exploit more selective conversion methods through controlling the complex reactions. In this paper, reaction mechanism of lignin pyrolysis studied by using dimeric lignin model compounds is presented focusing on four reactions, that is, depolymerization, polymerization, carbonization, and gasification.

Materials and method

Linkages between C₆-C₃ units in lignin are classified into several groups, that is, *β*-ether, *α*-ether, *β*-carbon bonding (*β*-1, *β*-5, *β*-*β*), biphenyl and so on. Eight dimeric lignin model compounds **1.8** (Fig. 1) were selected as model compounds for these structures and prepared. Model compound (10 mg) were placed in a bottom of a flask by evaporating the solution in MeOH, and the flask with cooling apparatus was heated in salt bath preheated at 400°C under atmospheric nitrogen for 1 min. After cooling, reaction system was extracted with THF (5 ml x 2), and the combined solution was evaporated to give THF-soluble fraction. Gas, THF-soluble and THF-insoluble fractions were determined by subtracting the weight of all apparatus from that before opening or extraction. THF-soluble fractions were characterized by GPC (Shodex KF-801, eluent: THF, Detector: UV₂₅₄) and HPLC (ODS-II, eluent: MeOH/H₂O, Detector: UV₂₅₄) analysis.

Results and discussion

Gas fraction directly indicates the gasification reaction, while THF-insoluble fraction obtained as black solids, which were not soluble in usual organic solvents and water, were considered to refer to the carbonization reaction. THF-Soluble fractions contained depolymerization and polymerization products as well as unreacted model compound as indicated by GPC and HPLC analysis. As a result, relative reactivity (Table 1) and degradation pathways (Fig. 1) of model compounds were clarified. Gasification was not important at 400°C, whereas carbonization occurred in almost model compounds even in the very stable biphenyl model compounds. These results indicate that carbonization occurs starting at the aromatic nuclei existing in all model compounds as common structural units via very reactive intermediates. As for polymerization, although *β*-O-4 types of model compounds gave polymerization products probably via quinonemethide types of intermediates, other model compounds scarcely gave polymerization products. Reactivity and pathways (Fig. 1) for depolymerization varied depending on the substructure; *β*-O-4, phenolic (ph) *β*-O-4 > non-phenolic (non-ph) *β*-O-4, non-ph *β*-1 >> ph *β*-1, biphenyl model compounds.

Consideration of the depolymerization behavior based on the present results by using the lignin molecule with 16 aromatic nuclei proposed by Adler [1] revealed that substantial depolymerization is observed when phenolic *β*-ether structure is cleaved. Although content of this structure is not large, such an effective depolymerization is due to successive generation from non-phenolic structures through cleavage of *β*-ether and phenolic *β*-ether structures.

Table 1. Reactivities of various lignin model compounds.

Substructure	Depolymerization*	Polymerization*	Carbonization	Gasification
<i>f</i> - Q 4	ph	• •	• >	• >
	non-ph	• •	• >	• ~
<i>f</i> - β 4	ph	• •	• ☞	• >
	non-ph	• >	• ~	• ☞
<i>f</i> - Α	ph	• ~	• ~	• •
	non-ph	• >	• ~	• ~
Bipheny	ph	• ~	• ~	• ☞
	non-ph	• ~	• ~	• ☞

*Depolymerization includes only cleavage of lignin main chain and does not include elimination of C^γ-carbon. Polymerization includes only reactions which give polymerization products soluble in THF.

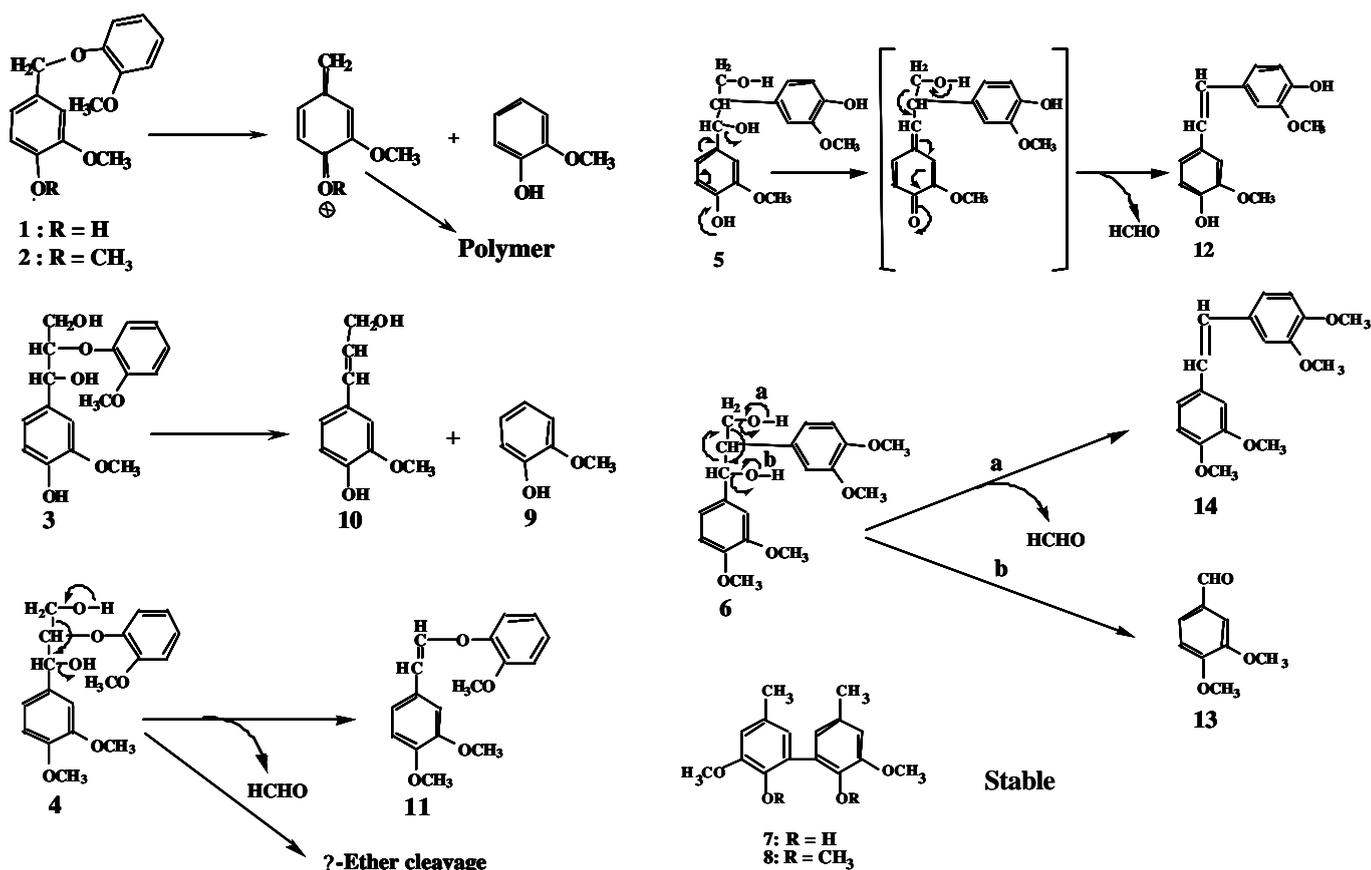


Fig. 1. Degradation pathways of lignin model compounds.

[1] E. Adler: *Wood Sci. Technol.*, **11**, 169 (1977).