Oxidative Cracking of Precipitated Hardwood Lignin by Hydrogen Peroxide*

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Abstract

Precipitated hardwood lignin (PHL) is a major byproduct in the biomass-to-ethanol process. Oxidative cracking of PHL by hydrogen peroxide in aqueous medium was investigated as a means to produce potentially useful chemicals. The cracking reaction takes place at moderate temperatures (80–160°C), giving mono- and dicarboxylic acids as the main products. The yields of these products are in the range of 30–50% of initial lignin. The reaction mechanism and the product distribution are dependent upon the reaction conditions, especially the pH. The reaction under strong alkaline conditions proceeds well even at low reaction temperatures (80–90°C). Under acidic conditions, higher temperatures (130–160°C) are required to attain the same degrees of cracking. The reaction patterns of the oxidative cracking reaction involve the cleavage of lignin ring, aryl ether bond, or other linkages within lignin. By using the findings of this investigation and those of previous work, we have illustrated the reaction pathways for degradation of PHL under alkaline and acidic conditions. Aldehydes and aromatic acids are intermediate products in the oxidative degradation of lignin. However, they were produced only in trace amounts owing to rapid degradation induced by hydrogen peroxide.

Index Entries: Lignin; oxidation; degradation; hydrogen peroxide.

Introduction

Lignin is a nonfermentable oxygenated aromatic polymer comprising generally 10–25% of the dry wt of lignocellulosic biomass (1). It is a major byproduct in the biomass-to-ethanol process. Yet, it is the least utilized

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component among the three major constituent polymers of biomass. Currently, lignin from ethanol plants is viewed primarily as a source of process fuel. Enhancing the value of lignin is a factor that could significantly affect the economics of the overall process.

Lignin is produced in various phases of the biomass conversion process. During the front end of the biomass processing, the feedstock is invariably put through a pretreatment process that usually involves treatment with dilute acid. A number of saccharification processes are currently being developed, solely on the basis of an acid catalyst. They include the “total hydrolysis” process of the National Renewable Energy Laboratory (NREL) (2), the ethanol plant of BC International (Jennings, LA), and the Arkenol Process (Mission Viejo, CA). All these acid-based pretreatment and saccharification processes are potential sources of a special grade of lignin. During the acid processes, a large fraction of the lignin is solubilized into the hot acidic medium, as high as 70% in the case of the NREL total hydrolysis process using hardwood. About one-third to one-half of this lignin is precipitated on cooling of the hydrolysate thus easily recovered. This lignin has many characteristics suitable for further conversion into various chemicals. It is a clean lignin, free of contaminants. It has low molecular weight, high solubility in various solvents, and high reactivity. Our investigation looks into the possibility of converting this lignin into low molecular weight chemicals. We focused on noncatalytic oxidative cracking of lignin in aqueous medium using H$_2$O$_2$.

Interest in reactions of hydrogen peroxide with lignin stems from the commercial use of this oxidant as a bleaching reagent in the pulp and paper industry. There has been a great deal of interest in the reactions of hydrogen peroxide with chromophoric and reactive groups in lignin. The action of hydrogen peroxide on lignin is not restricted to the interaction with chromophoric groups. It can also degrade and solubilize lignin, especially the reactive and low molecular weight lignin such as precipitated hardwood lignin (PHL). A study on the reaction of lignin with hydrogen peroxide can also reveal the characteristics of the PHL.

Hydrogen peroxide is a very weak acid that exists almost entirely in the undissociated form at pH < 9.0. At higher pH levels, hydroperoxide anions appear, and they are generally considered to be the reactive species in the oxidation reaction (3). The reactions of hydrogen peroxide with lignin are controlled by the type and distribution of inorganic and organic reactive species in the reaction mixture. The two most important factors are the pH of the reaction medium and the decomposition of the hydrogen peroxide (4). Depending on the pH, hydrogen peroxide acts as either a nucleophilic or an electrophilic species. It is stable under acidic conditions. Above pH = 6.0, the decomposition rate increases significantly and reaches its maximum at a pH equal to its pK$_a$ (11.6 at 25°C) (5) value, with a dismutation reaction as follows:

$$\text{H}_2\text{O}_2 + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{HO}^-$$