Oxidative Transformation of Wood and Lignin in the Alkaline Media: the New Mechanism and the Applied Aspects

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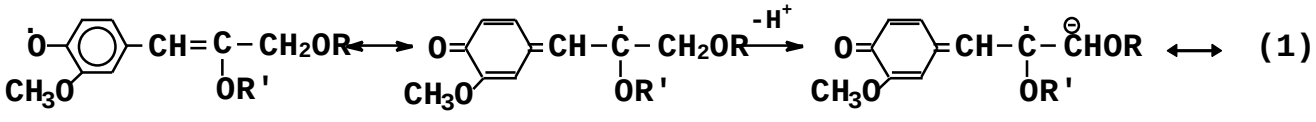
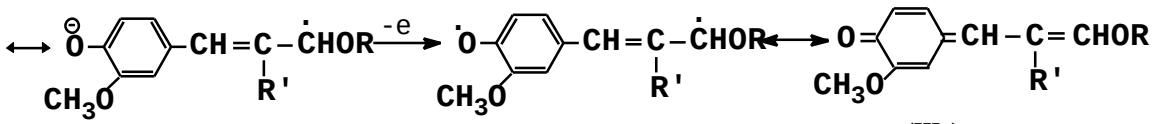
Alkaline oxidation of lignins could be applied for ecologically benign pulping and bleaching and for the vanillin and syringaldehyde production. These substances could be the main products under the convenient conditions [Taraban'ko V.E. e.a. Russ. Pat. No 2055831, 2055832, 2058291, 2059599, 2059600, 2059601, 2065434, 2072980]. None of described mechanisms of oxidation explains the role of alkali and involves directly the g-C-atom of propene chain of phenylpropene unit. On the other hand 60 years ago Hibbert suggested that the alkaline hydrolysis of lignin into vanillin carried out as the retrograde aldol reaction of a-hydroxy-g-carbonyl phenylpropene structure. If this idea were expanded on the oxidative processes, the role of oxidation should reside in formation of g-carbonyl group of the lignin phenylpropene unit. Such kind of mechanisms has not been discussed in literature yet.

In the present work the kinetics of oxygen consumption in the alkaline aspen wood oxidation has been studied. The reaction orders with respect to oxygen and original lignin of wood have been experimentally determined by analyzing the pH and oxygen pressure dependencies of initial rates of the process. The results obtained are discussed in terms of the theory of radical chain oxidation.

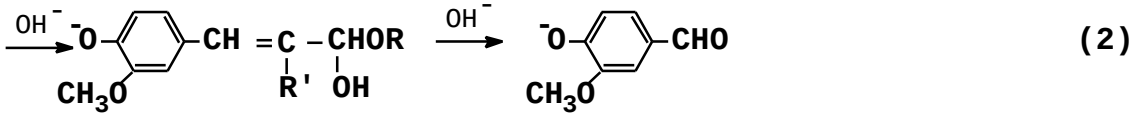
Oxidation of lignin and its model compounds in alkaline media is known to begin by the abstraction of electron from oxygen atom of phenolate anion followed by the partial removing of the radical center to b-carbon atom of propane chain (resonance structures (I), (Ia). To explain the known data we have suggested the possible mechanism of the transfer of the radical center from b- to g-carbon atom of propane chain. It is based on the known possibility of the acid dissociation of radicals (1). In this way the well known mechanisms of one-electron oxidation and retrograde aldol destruction of lignin structure (2) are pieced together:



(I) (Ia) (II) (1)



(IIa) (III) (IIIa)



(IV) (V) (2)

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