# Catalytic nitrobenzene oxidation of lignins

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Alkaline nitrobenzene oxidation of hardwood and softwood lignins in the presence of redox and phase-transfer catalysts was studied. The selectivity of oxidation of lignins increased by 1.7 to 1.9 times. A possible mechanism of catalysis is discussed.

**Key words:** aromatic aldehydes, syringaldehyde, vanillin, softwood, hardwood, lignin, catalysts, nitrobenzene oxidation.

Alkaline nitrobenzene oxidation (ANBO) is a general method for the study of the structure and transformations of lignin under certain conditions.[1] The high selectivity of nitrobenzene (NB) as an oxidant for lignin, which makes it possible to synthesize aromatic aldehydes through degradation of this polymer, is of practical importance. Manufacture of vanillin still remains one of a few examples of the rational utilization of lignin, which is a large-tonnage waste of modern chemical pulp processing technology,[2] and the highest yields of aromatic aldehydes are obtained upon oxidation of lignins from the initial wood.[3,4] Of the technical lignins, only lignosulfonates give an economically acceptable yield of vanillin (>10%) upon oxidation. Since the production of aldehydes from lignin is a multistep process and is accompanied by significant losses at different stages of manufacture,[5] it is natural that an increase in the yield of target products in the first step of the process, *viz.*, in alkaline oxidation, is desirable. The alkaline nitrobenzene method provides vanillin in a yield of >20% with respect to lignin upon oxidation of softwood and a mixture of vanillin and syringaldehyde in a >40% yield upon oxidation of hardwood lignins.[1,3,4,6,7]

Alkaline nitrobenzene oxidation is a liquid-phase process, where NB is an oxidant. Surprisingly, the intense development of processes of liquid-phase oxidation of organic compounds in the last decades[8] did not involve the rather selective process of lignin oxidation with NB, in particular, the use of catalysts. Anthraquinone (AQ)[9] and *o*-phenanthroline (*o*-P)[10,11] are catalysts widely used for oxidation of lignin with oxygen and hydrogen peroxide in delignification and bleaching.

With the above data in mind, we assumed that the use of catalysts in ANBO as the oxidation process would make it possible to increase the yield of aromatic aldehydes from lignin and, hence, the value of ANBO as a method of analysis of lignin. This assumption is based on the results of ANBO of aspen wood obtained by us previously.[12,13]

We used the above catalysts for ANBO of hardwood lignins: aspen (*Populus tremula*) and birch (*Betula verrucosa*), and softwood lignins from pine (*Pinus sylvestris*) and larch (*Larix sibirica*).

## Experimental

Wood flour of aspen, birch, pine and larch (moisture content 6%) extracted with an ethanol—benzene mixture were subjected to oxidation. ANBO of wood was carried out using the classical K. Freudenberg procedure described previously[14]. A batch of wood was taken with account of the content of Klason lignin in wood and referred to 1.00 g of lignin (aspen, 4.78 g of dry wood; birch, 4.65 g; pine, 3.65 g; larch, 3.33 g) and placed into an autoclave. A 2 *M* aqueous NaOH solution (37.5 mL), NB (2.1 mL), and a calculated amount of catalyst were added. The mixture was thoroughly stirred, the autoclave was sealed and kept for 3 h in an oil bath at 170±2 °C with vigorous stirring. When the process was completed, the autoclave was cooled, the alkaline mixture was filtered to remove traces of wood and the products of reduction of NB, and the precipitate on the filter was washed with a small amount of water. The washing and the alkaline filtrate were combined and extracted three times with benzene to remove traces of NB and its reduction products. The extract was discarded, and the alkaline solution was acidified to pH 2 and extracted again three times with benzene to isolate aromatic aldehydes from the reaction mixture. The extracts were combined, dried over sodium sulfate, and concentrated. The products were analyzed by GLC with a Chrom-5 chromatograph equipped with a katharometer as the detector, a column (1.2 m) with 3% of PEGA and 1% of $H_3PO_4$ on Chromosorb NaW-AW; the temperature was programmed from 90 to 250 °C (8 deg $min^{-1}$). He was used as the carrier gas (60 mL $min^{-1}$). For quantitative analysis, naphthalene was used as the internal standard.

## Results and Discussion

A characteristic feature of AQ as a catalyst of delignification is that not the AQ itself, but rather an AQ—AHQ (anthrahydroquinone) redox system has cata-

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lytic properties. AHQ is formed due to reduction of AQ under conditions of alkaline cooking with carbohydrate components of the plant complex.[15] The reduction of AQ to AHQ with lignin, *i.e.*, the oxidation of lignin with anthraquinone, is not documented. The positive action of the AQ—AHQ system in alkaline delignification is of dual character.[15] First, it intensifies fragmentation of lignin by reacting with the quinonemethide elements of this polymer; second, it plays the role of a reducing agent and deactivates the reactive phenoxyl radicals formed in the alkaline medium, thus preventing coupling and condensation of lignin.

The results of oxidation of wood with NB in alkaline medium in the presence of AQ and *o*-P are listed in Table 1. It can be seen that the addition of a catalyst to the reaction mixture increases the yield of aldehydes (mainly, syringaldehyde for hardwood) in the whole range of concentrations of catalysts with a pronounced maximum. Alkaline degradation of lignin in the absence of AQ is accompanied by oxidative transformations of the side chain of lignin with the formation of ketone groups at the α-carbon due to traces of oxygen dissolved in the alkali. Therefore, nitrobenzene oxidation (NBO) of soda lignins produces a decreased yield of aldehydes.[16] A similar result was also obtained for oxidation of soda-anthraquinone lignins, however, the presence of both AQ and NB in the reaction mixture increases the yield of aldehydes, which suggests the existence of conjugated redox processes. It is known[17] that prereduction of lignin increases the yield of aromatic aldehydes in ANBO.

It is believed that the mechanisms of action of *o*-P and AQ as catalysts of alkaline delignification are different.[10,15] At present, the authors, who proposed *o*-P as a catalyst for oxygen-alkaline delignification, explain the catalytic properties of this compound by its high complex-forming activity.[10]

**Table 1.** Dependence of yield of aromatic aldehydes (%) in alkaline nitrobenzene oxidation of lignins on the percentage of a catalyst

| Percentage of catalyst (%) | Aspen* | | Birch* | Pine** | Larch** |
|---|---|---|---|---|---|
| | Anthraquinone | *o*-Phenanthroline | *o*-Phenanthroline | | |
| 0 | 39.1/31.0 | 39.1/31.0 | 51.0/39.0 | 19.0 | 18.7 |
| 0.5 | 45.2/37.0 | 44.9/35.6 | 53.3/41.1 | 20.3 | 19.3 |
| 1.0 | 50.2/41.1 | 56.5/45.8 | 55.2/41.4 | 22.1 | 20.0 |
| 1.5 | 51.0/41.5 | 58.5/47.6 | 56.1/42.1 | 23.0 | 20.6 |
| 2.0 | 52.0/42.3 | 58.8/48.0 | 56.4/42.6 | 23.5 | 20.8 |
| 2.5 | 54.0/43.9 | 59.2/48.5 | 57.3/43.5 | 25.3 | 21.4 |
| 3.0 | 56.9/46.2 | 61.8/50.5 | 58.0/44.2 | 26.1 | 21.8 |
| 3.5 | 63.1/53.2 | 64.7/53.6 | 66.2/52.2 | 26.9 | 22.0 |
| 4.0 | 58.1/48.7 | 49.7/40.0 | 59.3/45.4 | 27.4 | 22.1 |
| 4.5 | 52.6/43.5 | 48.4/39.8 | 54.0/42.0 | 36.0 | 22.2 |
| 5.0 | 51.3/42.2 | 46.0/38.0 | 52.0/40.4 | 26.0 | 32.2 |
| 5.5 | — | — | — | 21.0 | 24.9 |
| 7.5 | — | — | — | | 22.7 |

* The total yield of vanillin and syringaldehyde is given in the numerator, and the yield of syringaldehyde is given in the denominator. ** Yield of vanillin.

However, in the case of oxidation of lignin with NB, the effects of AQ and *o*-P were identical (see Table 1). This makes it possible to assume that under conditions of the process, *o*-P undergoes transformations similar to those for AQ *i.e.*, *o*-P is primarily reduced to dihydrophenanthroline, which subsequently reacts with lignin and, probably with NB analogously to AQ—AHQ. We have no data for ruling out the complex-forming mechanism of action of *o*-P, but the decrease in the yield of aldehydes in NBO after the maximum point suggests another interpretation of the catalytic action of *o*-P in redox processes; possibly, the reduced form, dihydrophenanthroline, plays a definite role. Thus, AQ and *o*-P act as inhibitors of oxidation in ANBO of wood lignins.[8,18]

A mechanism of degradation of lignin during alkaline delignification in the presence of AQ as the catalyst for phenolic and nonphenolic units of the substrate was presented.[15,19]

Under the action of high temperature and alkali, the phenolic fragments of lignin transform into a quinonemethide form, which reacts with AHQ and causes intense disintegration of the polymer, yielding a large number of low-molecular-weight compounds, which are substrates for NBO. For the nonphenolic fragments of lignin, alkaline degradation in the presence of AQ—AHQ proceeds *via* intermediate stilbene structures, which decompose by the mechanism of retroaldol condensation; it causes in part the formation of low-molecular-weight nonphenolic aldehydes, and some of them are similar to the target products. Probably, the products of reduction of NB, which are present in the reaction mixture, favor the transformation of nonphenolic fragments into phenolic ones.

Intensification of alkaline degradation of lignin in the presence of AQ results in the formation of a series of monomeric compounds, such as coniferyl and sinapyl alcohols and aldehydes, *i.e.*, isoeugenol, propenylsyringol, vinylguaiacol, and vinylsyringol, which are oxidized quantitatively with NB at the double bond into vanillin and syringaldehyde.[1]

It should be noted that the presence of NB in alkaline delignification increases the yield of cellulose, and decreases the residual content of lignin in the fiber, *i.e.*, improves the cooking process[20]. It was established empirically that additives for the cooking solution, which improve the process of alkaline delignification, also favor an increase in the yield of aldehydes in oxidation of lignin, and *vice versa*. Thus, NB in the process under study not only plays the role of an oxidant, but also an additive improving delignification.

The analysis of the data in Table 1 shows that the tendencies in the increase and decrease in the yield of aldehydes on approaching and passing through the maximum are similar for all lignins studied. Thus suggests

**Table 2.** Dependence of the percentage of *o*-phenanthroline required for the maximum yield of aldehydes on the content of lignin in the sample

| Wood species | Content of lignin | Percentage of *o*-P | Catalyst/lignin content ratio |
|---|---|---|---|
| | (% of wood) | | |
| Aspen | 20.9 | 3.5 | 0.167 |
| Birch | 21.5 | 3.5 | 0.163 |
| Pine | 27.4 | 4.5 | 0.164 |
| Larch | 30.0 | 5.0 | 0.167 |

**Table 3.** Dependence of the yield of aromatic aldehydes in ANBO of aspen wood on the composition of the oxidative mixture

| Composition of catalyst* (% of wood) | Yield of aldehydes (% in relation to lignin) | |
|---|---|---|
| | Syringaldehyde | Syringaldehyde + vanillin |
| 0:0 | 31.0 | 39.1 |
| 3.5:0.84 | 61.5 | 74.5 |
| 3.5:0 | 53.6 | 64.7 |
| 0:0.84 | 37.6 | 48.2 |
| 3.13:3.35 | 61.5 | 74.5 |
| 2.00:1.68 | 55.0 | 67.0 |
| 4.50:16.81 | 48.2 | 59.1 |
| 3.50:0.42 | 57.3 | 67.5 |
| 5.00:0.84 | 45.0 | 55.5 |
| 2.50:0.52 | 43.6 | 53.9 |
| 0.25:0.52 | 35.6 | 44.0 |
| 0.50:0.84 | 41.4 | 51.0 |

* *o*-P:PEG ratio.

that a definite correlation exists between the lignin content in wood and the amount of the oxidation catalyst (Table 2).

In fact, the ratios of the amount of catalyst at the point of the maximum yield of aldehydes and the percentage of lignin in the wood are the same, *i.e.*, one can conclude that the increase in the yield of aldehydes in NBO in the presence of the above catalysts is a general phenomenon for all lignins independent of the wood species.

The functional and structural characteristics of aspen and larch lignins isolated from milled wood with a 9:1 dioxane—water mixture were studied by $^1$H and $^{13}$C NMR.[21] It was shown that the sample of aspen contains 58% of syringyl, 28% of guaiacyl, and 14% of *p*-hydroxyphenyl structures, and larch contains 87% of guaiacyl and 13% of dihydroxyphenyl nuclei per 100 aromatic rings.

In addition, it should be noted that at the point of the maximum yield of vanillin in oxidation of larch wood, protocatechualdehyde was detected by chromatography in a yield of *ca.* 10%. This compound was not detected in oxidation without catalysts.

Recently, the use of phase-transfer catalysts has attached great attention. It is known that tetraalkylammonium salts, crown ethers, and polyethylene glycols (PEG) of different molecular weight are used as phase-transfer catalysts.[22]

We studied PEG-400 as a catalyst, whose use allowed increasing the yield of aldehydes in ANBO of aspen wood lignin.[23,24] The compositions of different oxidative mixtures based on NB and containing both a redox catalyst (*o*-P) and a phase-transfer catalyst (PEG-400) in different proportions are presented in Table 3. As can be seen from Table 3, the maximum yield in ANBO obtained using *o*-P, can be increased by using PEG as the phase-transfer catalyst with minimum consumption of the latter (*ca.* 0.8 wt. % of wood). The total yield of aldehydes attains *ca.* 75%, and syringaldehyde is obtained in a yield of 61.5%; the synergistic effect of the catalysts is evident. This result is in agreement with that obtained in previous studies,[1] although the yield of syringaldehyde is higher than that published previously.[2] This discrepancy can be explained by the fact that in this case oxidation of wood lignin as a whole, not its fraction, occurred. Studies of oxidation of preliminary extracted spruce wood and dioxane-extracted spruce lignin with copper oxide under identical conditions show that wood flour is a better starting material for studies of the structure of lignin than isolated lignin.[25]

The positive effect of the phase-transfer catalyst PEG-400 in the absence of *o*-P can be explained by the formation of a complex of $Na^+$ with PEG, which transforms the alkaline medium used (2 *M* NaOH) into superbasic one (PEG—NaOH). This transition is identical to an increase in the basicity of the medium. In fact, in 3 *M* NaOH, the maximum yield of aldehydes in oxidation of lignin was observed, all other conditions being equal.

Thus, for the first time in the chemistry of lignin, we have developed two- and three-component NB-containing compositions, which allow strikingly increasing the efficiency of ANBO of lignins.

The use of catalytic ANBO is advantageous for the study of the potential of lignin-containing raw materials for manufacturing aromatic aldehydes and also gives additional information on the structure of lignins from different wood species.

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