

Study of Mechanism and Improvement of the Process of Oxidative Cleavage of Lignins into the Aromatic Aldehydes

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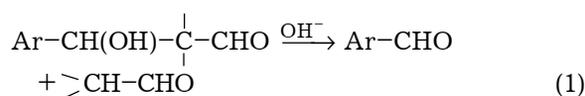
Abstract

Known hypotheses concerning the mechanism of formation of aromatic aldehydes (vanillin and syringaldehyde) in the processes of oxidative cleavage of lignins are discussed. A new mechanism of lignin oxidation is described, which starts from the formation of phenoxy radical and is completed by the formation of vanillin through the retro-aldol cleavage of substituted coniferyl aldehyde. Oxidation of the model compounds is studied and experimental confirmations of the proposed mechanism are obtained. Coniferyl alcohol, the postulated intermediate of eugenol oxidation, was detected by GC-MS. Comparison of the kinetics and oxidation products of vanillidenacetone and lignosulphonates, eugenol and isoeugenol, guaiacyl ethanol and quaiacyl propanol confirms the proposed mechanism. On its basis, possibilities are found to elevate the selectivity of lignin oxidation by oxygen into aromatic aldehydes by accelerating the process due to tightening conditions.

INTRODUCTION

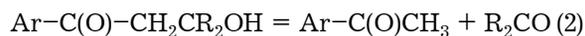
The problem connected with processing of wood and other renewable plant resources into the products of traditional organic synthesis has the history almost a century long. In spite of enormous potential accumulated in this area, attention to it increases during the recent years because sustainable development of the civilization in future requires anticipatory transfer of the raw material basis of chemical industry to renewable plant raw material [1–4]. Among the variety of these processes, the oxidation of lignins into vanillin is distinguished firstly by the fact that this production had been realized on industrial scale in the 30–40ies of the past century [1]; however, on the other hand, large number of published hypotheses concerning the mechanism of oxidative cleavage of the phenyl-propane structural unit of lignin into aromatic aldehydes does not allow explaining even the basic, well known regularities.

Lignin is one of the main polymeric components of wood and a large-scale waste product of pulp and paper industry. The basis of its structure is the so-called phenyl-propane structural unit (PPU). Oxidation of softwood lignins in alkaline medium results in obtaining vanillin; processing the lignosulphonates with this purpose had been organized on industrial scale in the 30–50ies of the 20th century [1, 2]. The first hypothesis about the mechanism of vanillin formation was formulated by Hibbert [5]. He assumed that during alkaline hydrolysis of lignosulphonates in the absence of oxidants vanillin is formed by retro-aldol cleavage of α -hydroxy- γ -carbonyl structure of the phenyl propane structural unit of lignin in alkaline medium:

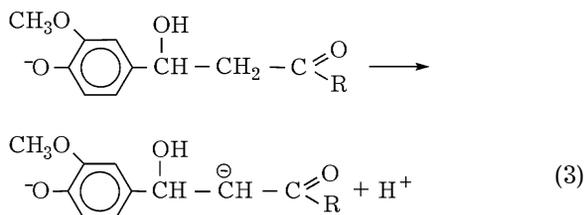


where Ar is 3-methoxy-4-phenoxy anion. The indicated scheme provides a good description

of alkaline hydrolysis of lignin without oxidants with the formation of vanillin. First, it allows explaining the formation of the corresponding aceto derivatives, acetovanillone and acetosyringone, as by-products of alkaline hydrolysis of lignins in a similar process of the hydrolysis of α -carbonyl structure [5, 6]:

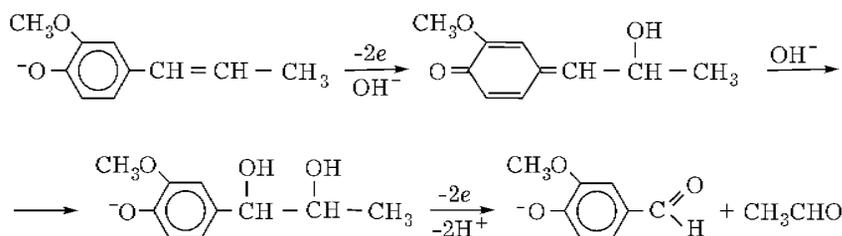
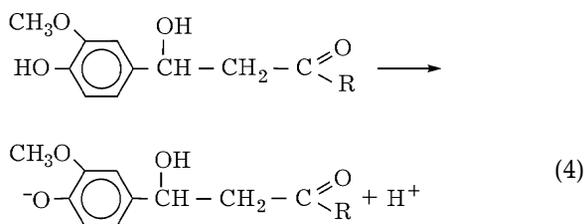


Second, reactions (1), (2) require strongly alkaline medium, because the formation of double-charged enolate ion, which is necessary for aldol condensation and cleavage processes [7], is a result of the dissociation of phenolate anion of PPU:



It is evident that the constant of dissociation (3) is several orders of magnitude smaller than that for the dissociation of phenol group of PPU and methylene group of neutral γ -oxy-carbonyl structures. Weakly alkaline medium is quite sufficient for the hydrolysis of the latter [8].

The pK values for model lignin compounds are 9–10 and more [9, 10]. So, efficient progress of reactions (1), (2) is possible only in a medium much more alkaline than that necessary for the acidic dissociation of phenol groups of lignin (4) or retro-aldol cleavage of neutral molecules.



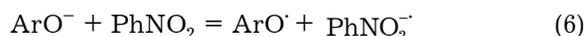
Maximal vanillin yield in the processes of alkaline hydrolysis is within the range 5–6 % of lignin mass [1, 5, 6]. Under the action of the most active oxidants, nitrobenzene and copper (II), the yield of aromatic aldehydes increases by a factor of 5–10 and can exceed 40–50 % (molar fraction) [11–13]. Oxidation by oxygen also increases the yield of oxyaldehydes both in the presence of catalysts and in their absence [4, 14, 15]. Almost in all the cases, the formation of aldehydes is accompanied by the corresponding aceto derivatives as by-products [11, 14, 15]. High vanillin yield in the oxidative processes is possible only in alkaline media [6, 14, 16].

In our viewpoint, the mentioned facts indicate that the selective formation of vanillin and syringaldehyde from lignin in alkaline media proceeds *via* the mechanisms having common features, first of all the stage of retro-aldol cleavage, without any substantial dependence on oxidant nature. Nevertheless, attempts to use retro-aldol cleavage reactions (1), (2) as the final step for the analysis of oxidation mechanisms have not been made until recently.

In spite of the detailed and lengthy study of the oxidation of lignin and its model compounds by nitrobenzene [1, 6, 13, 14, 16], only a few works deal with the mechanism of this process. A two-electron mechanism of isoeugenol oxidation by nitrobenzene (scheme (5)) is proposed in monograph [16]. According to this mechanism, the cleavage of the C–C bond proceeds similarly to the cleavage of bond in 1,2-glycols under the action of iodic acid [7]. This hypothesis has some shortcomings: first, oxidation through quinone methides leads to the addition of hydroxyl in α - (kinetic control) or in γ -position (thermodynamic control), but not in β -position [17, 18]; second, oxidation by iodic acid proceeds in acid media, while vanillin is formed in alkaline ones; finally, scheme (5) cannot explain the formation of aceto derivatives.

A more detailed analysis of the mechanism of nitrobenzene oxidation of lignin and its model compounds is described in [19].

Nitrobenzene acts as a one-electron oxidant in the oxidation of phenol and other compounds, as well as in photooxidation [19, 10]. According to [19], the process starts not with electron transfer from the phenol oxygen of phenolate anion to oxidant molecule



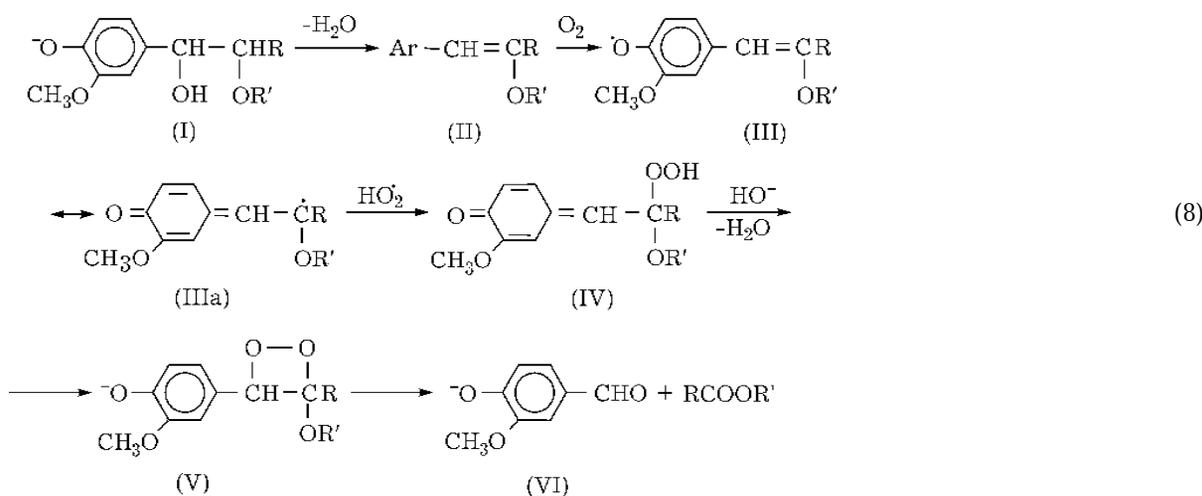
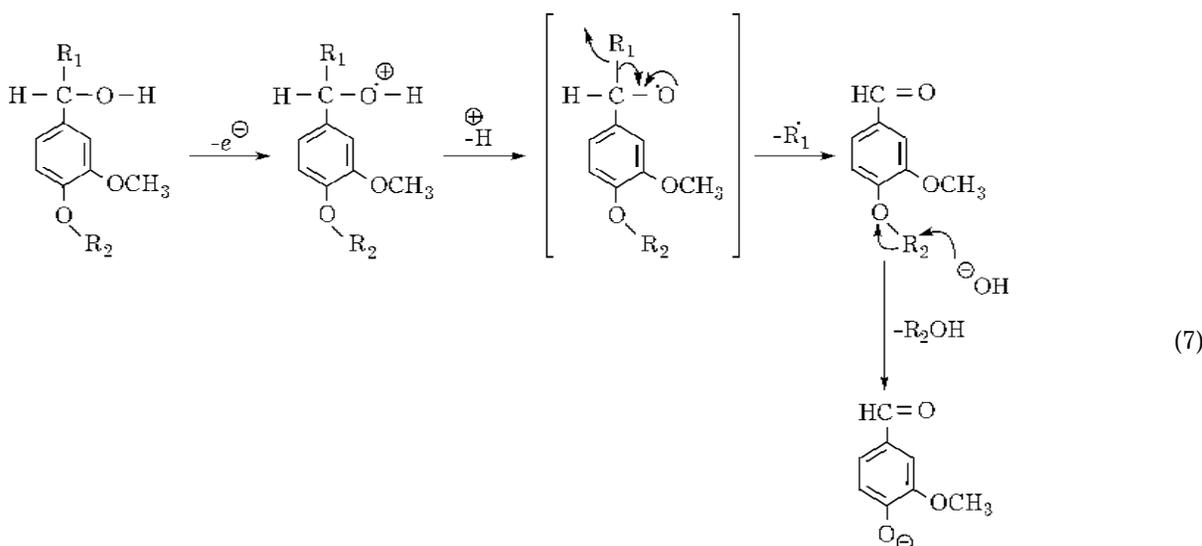
but with electron detachment from the hydroxyl of the benzyl group of phenyl-propane unit, independently of the presence or absence of free phenol hydroxyl in the molecule under oxidation (scheme (7)).

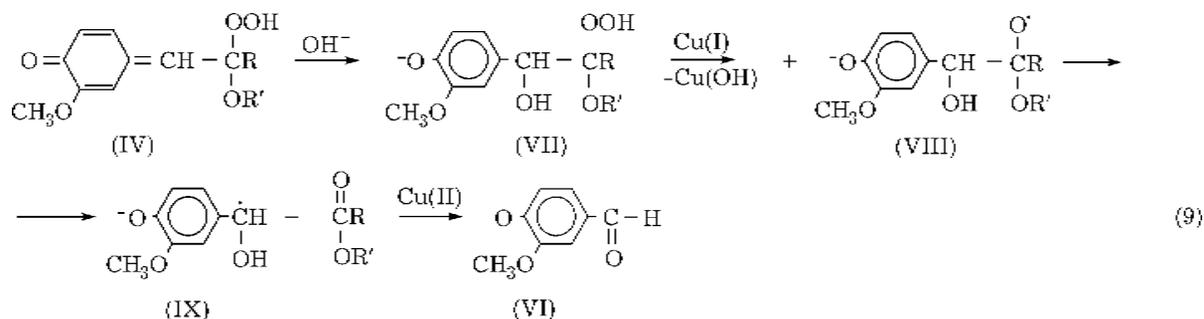
This assumption is principally different from the predominant notions that the processes of this type proceed through the formation of

quinone methide intermediates (see below). As regards the experimental confirmations of hypothesis (7) [19], they can be also interpreted with hypotheses (6) and (7) with the same success.

Oxidation mechanism including quinone methide intermediates (III)–(IIIa) and dioxethane (V) as key intermediates (scheme (8)) is proposed in [21, 22] where the problem of oxygen alkaline bleaching of cellulose is considered. A similar hypothesis was used to describe the mechanism of lignin oxidation during obtaining aromatic aldehydes from hardwood [23].

Decomposition of dioxethane (V) is likely to proceed by synchronous cleavage of C–C and O–O bonds leading to the formation of vanillate ion (VI). It should be specially noted that the authors of [23] accepting scheme [22]





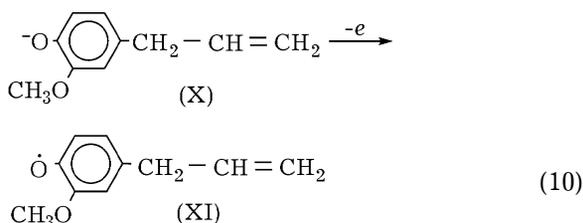
to describe the mechanism of aromatic aldehyde formation did not provide any comments for the known fact that the yield of aldehydes increases under the action of copper catalysts, though the major experiments have been carried out with these catalysts [23]. This means that the authors of [23], who propose the mechanism of vanillin formation (8), restrict the role of catalyst to the acceleration of the stage involving oxidation of substrate (II) by oxygen, which does not allow one to explain the growth of selectivity of the process under the action of catalyst. In addition, scheme (8), similarly to the majority of hypotheses under consideration, does not provide an explanation to the formation of aceto derivatives as by-products.

The scheme combining the formation of quinone methide hydroperoxide (IV) and the known regularities of the catalytic decomposition of hydroperoxides was proposed in [4, 24, 25] (scheme (9)). This scheme allows explaining the effect of the catalyst on the process rate, but it does not explain the formation of aceto derivatives and the necessity for strongly alkaline medium. A discrimination experiment planned and carried out later (vanillin oxidation at low pH does not result in the formation of the product of dimerization of (IX) as predicted by scheme (9)) did not confirm this hypothesis [26].

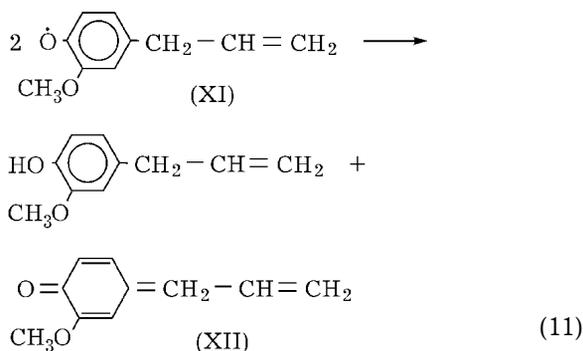
So, despite substantial differences between the considered hypotheses on the mechanism of oxidative cleavage of lignins into aromatic aldehydes, they have a common shortcoming: the absence of any explanation of the necessity to use strongly alkaline media for the process and of the formation of aceto derivatives as by-products.

The mechanism providing such an explanation is proposed in [27–29]. According to the

scheme shown below for eugenol as an example, oxidation starts with electron detachment from phenoxyl anion (X):

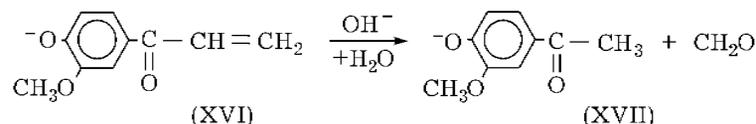
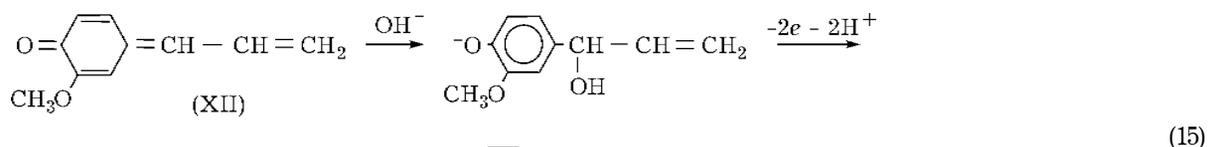
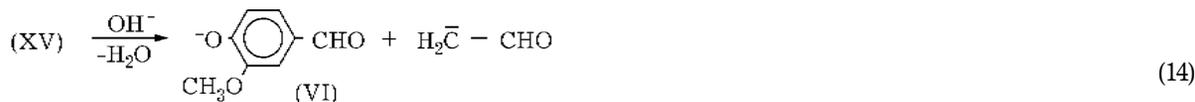
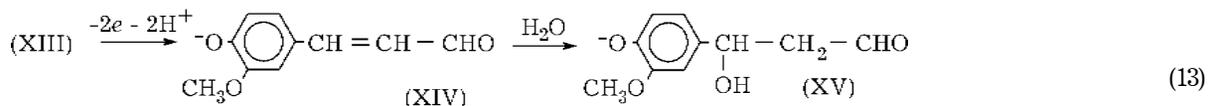
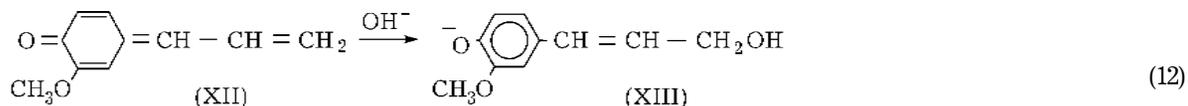


Disproportionation of primarily formed phenoxyl radicals (XI) gives quinone methide (XII):



while nucleophilic addition of hydroxide ion to it forms the structure of coniferyl alcohol (XIII) (scheme (12)). During subsequent oxidation of coniferyl alcohol (XIII) according to scheme (13), γ -carbonyl group is formed (XIV). Retro-aldol cleavage of α - β -unsaturated aldehyde (XV) gives vanillin (VI) (scheme (14)).

The proposed mechanism explains also the formation of aceto derivatives as admixtures through the addition of hydroxide anion to α -position of quinone methide (XII) followed by retro-aldol cleavage of α -carboxyethylene structure (XVI) (scheme (15)). It is known that under thermodynamic control the addition of nucleophilic agents to quinone methides occurs into the γ -position; this allows explaining the nature of the main (vanillin, thermody-



namic control) and by-product (acetovanillone (XVII)).

All the listed intermediates and their transformations into each other are characteristic of lignin chemistry [14, 16, 18]. It was assumed that the transformation of phenoxyl radical into quinone methide can proceed not only through the disproportionation stage (11) but also through CH-acidic dissociation of radical (XI) followed by the oxidation of the resulting anion radical [30].

The goal of the present work is experimental confirmation of the proposed oxidation mechanism (10)–(15) [27–30].

EXPERIMENTAL

Fermented spent sulphite liquor from the Syas' PPP (Leningrad Region) obtained from fir wood by sulphite cooking with sodium base contained 42.6 mass % dry substances. The composition of the dry substances of lye, %: ash – 18.3, hydrogen – 5.26, carbon – 40.5, sulphur – 6.05, lignin – 65.

Eugenol with the main substance content above 98 % manufactured by JSC Aromasintez (Kaluga city) was used. Vanillidenacetone (VA) was obtained by croton condensation of vanillin and acetone in alkaline medium [28].

Guaiacyl ethanol and guaiacyl propanol were synthesized from vanillin and the corresponding alkyl magnesium iodide [31].

The NMR ^{13}C spectra of vanillidenacetone were recorded at +25 °C with Bruker AM-400 spectrometer (100.61 MHz) associating with the deuterium resonance of the solvent. Chemical shift was calculated with respect to the signal of solvent (CDCl_3) using it as an internal standard: δC 76.90 ppm. ^{13}C NMR: δ 27.0 (C- δ , methyl of the acetate), 55.7 (C methoxyl), 109.4, 114.8 (C- β , C- α , CH=CH), 123.2, 124.6 (C-2, C-6, CH aromatic), 126.6 (C-1, aromatics), 143.7 (C-5, C-H aromatic), 146.7, 148.9 (C-3, C-4, aromatics).

Mass spectrum of VA corresponds to that from the Finigan MAT NIST data base for GCQ/ICIS: M^+ 192 (80), 191 (45), 177 (70), 175 (30), 145 (100), 118 (20), 89 (20), 77 (7).

Oxidation of lignosulphonates and model compounds was performed at 160 °C in a steel swinging reactor with argon or oxygen partial pressure of 0.3 MPa. Oxygen was admitted into the reactor from a calibrated buffer vessel through a special valve as it was absorbed in the reactor, as described in [15, 24, 28]. Concentrations of the compounds to be analyzed were determined by means of GLC after acidifying and extraction of the samples. Copper hydroxide was used as a catalyst (10 g/l) for

the oxidation of vanillidenacetone by oxygen, similarly to the oxidation of lignosulphonates.

RESULTS AND DISCUSSION

The data on the effect of alkalinity of the medium on vanillin yield and rate of oxygen absorption during the oxidation of lignosulphonates are shown in Fig. 1. A decrease in pH from 10.7 to 10.1 leads to almost complete suppression of vanillin formation process but has almost no effect on oxygen absorption at 160 °C. The rate of phenol and lignin oxidation is known to diminish with a decrease in pH due to decreasing the acid dissociation degree; however, cessation of oxygen absorption due to this reason occurs at much lower pH (9–9.5) [25]. Therefore, suppression of vanillin formation when decreasing pH of the medium is not connected with the protonation of phenol

hydroxyl leading to cessation of oxidation at pH 9–9.5, but is due to acid dissociation of the process intermediates, which are less acidic than phenols. In the mechanism involving (9)–(14), such a reaction is the stage of retro-aldol cleavage of substituted coniferyl aldehyde (XIV). It should be noted that this fact, easily explained by the proposed mechanism (see Fig. 1), has no explanation in other known hypotheses.

To confirm the role of retro-aldol cleavage in the formation of vanillin, we studied chemical behaviour of vanillidenacetone under the conditions of lignosulphonate oxidation. Unlike coniferyl aldehyde, vanillidenacetone is easily synthesized from vanillin and acetone and depicts rather accurately the structure of phenyl propane unit in the γ -carbonyl form (XIV).

In the argon atmosphere, vanillidenacetone is hydrolyzed with the formation of vanillin at pH 10 and 160 °C for 30–50 min, selectivity with respect to vanillin being about 90 % at the initial region (Fig. 2). In the presence of oxygen and the catalyst, vanillideacetone is consumed faster and vanillin yield decreases by a factor of 3–5 (see Fig. 2, a). This means that at pH 10 the rate of retro-aldol cleavage is less than the rate of vanillidenacetone oxidation into by-products, which is the reason of a substantial decrease in vanillin yield under the action of oxygen. With pH increased to 11, the situation changes due to an increase in the rate of retro-aldol cleavage, which is proportional to the concentration of hydroxide ion [28, 32]: a maximal vanillin yield does not decrease under the action of oxygen, and the selectivity of its formation before achieving the maximum exceeds 80 % (see Fig. 2, b). A decrease in vanillin yield after attaining its maximal concentration is likely to be due to its subsequent oxidation. The effect of pH on vanillin yield from the oxidation of lignosulphonates is similar (see Fig. 1). Thus, the comparison shows that retro-aldol cleavage of the substituted coniferyl aldehyde (XIV) plays an important role in the oxidation of lignosulphonates, while at pH below 10–11 it limits the process of vanillin formation.

A similar dependence of vanillin yield on pH is observed also for non-catalytic oxidation of eugenol at 170 °C (Fig. 3). A transition from

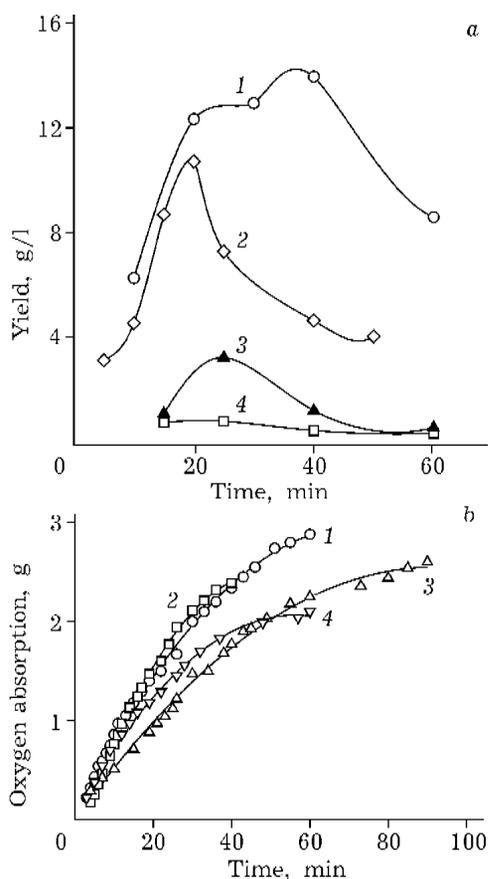


Fig. 1. Effect of pH on vanillin yield (a) and oxygen absorption (b) at 160 °C: 1 – 120 g/l NaOH; 2 – 80 g/l NaOH; 3 – 40 g/l NaOH + 300 g/l K_2CO_3 ; pH 10.7; 4 – 300 g/l K_2CO_3 , pH 10.1.

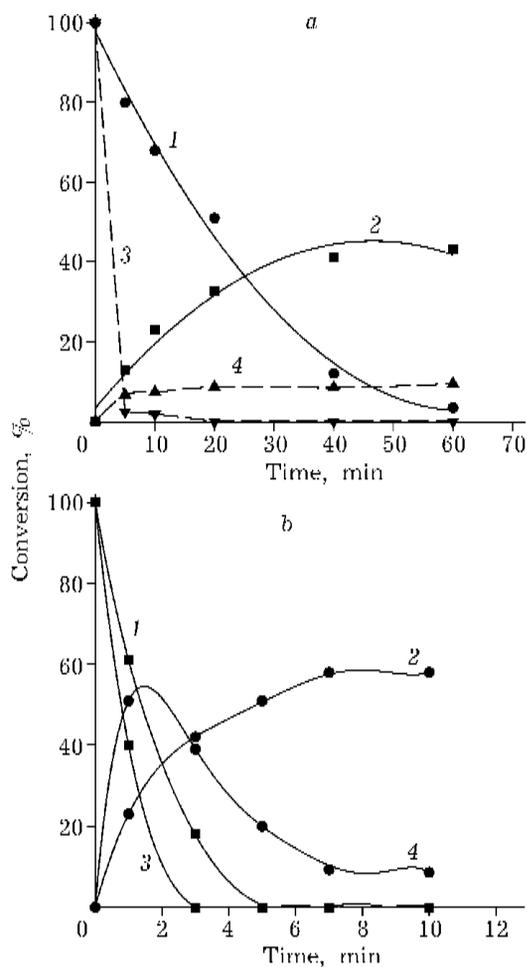


Fig. 2. Kinetic curves of VA consumption (1, 3) and vanillin accumulation (2, 4) in argon (1, 2) and oxygen in the presence of copper hydroxide (3, 4) at pH 10 (a) and 11 (b). Process conditions: 10 g/l VA, 160 °C, argon or oxygen partial pressure 0.3 MPa.

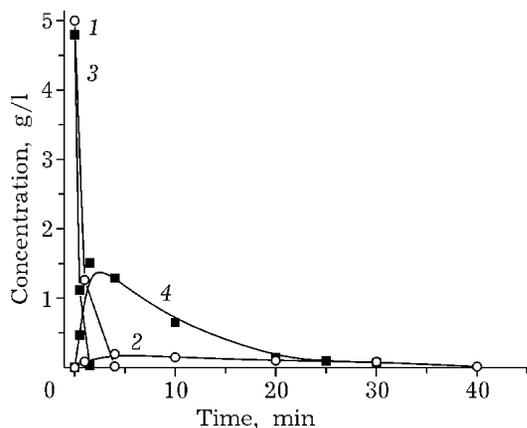


Fig. 3. The curves of vanillin accumulation (2, 4) and substrate consumption (1, 3) for eugenol oxidation by molecular oxygen at pH 10 (1, 2) and in 1 M NaOH (3, 4) without catalyst (160 °C, 5 g/l eugenol, 0.3 MPa O₂).

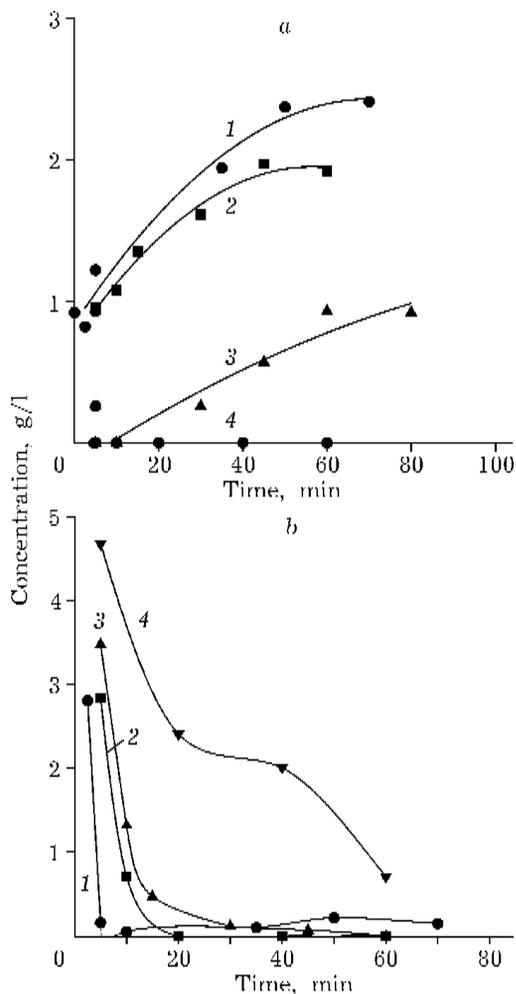


Fig. 4. The kinetics of vanillin accumulation (a) and eugenol consumption (b) under oxidation with oxygen in the presence of 10 g/l copper oxide (160 °C, 5 g/l eugenol, 0.3 MPa O₂): 1 - 1 M NaOH; 2 - pH 11; 3 - pH 10; 4 - pH 9.

1 M NaOH solution to pH 10 leads to a 5–7-fold decrease in vanillin yield. A similar decrease in vanillin yield is also observed during the catalytic oxidation of eugenol at 160 °C (Fig. 4). Unlike lignosulphonates, a decrease in alkalinity is also accompanied by a decrease in oxygen absorption rate (Fig. 5). This fact indicates that eugenol is protonated within pH 10–11. Really, eugenol acidity at 20 °C is characterized by pK 10 [9, 10].

Selectivity of eugenol oxidation into vanillin does not exceed 10–40 % (molar fraction) at the initial regions of the kinetic curves; vanillin is formed in noticeable amount also after complete consumption of eugenol (see Fig. 3, 4). This means that vanillin is formed in

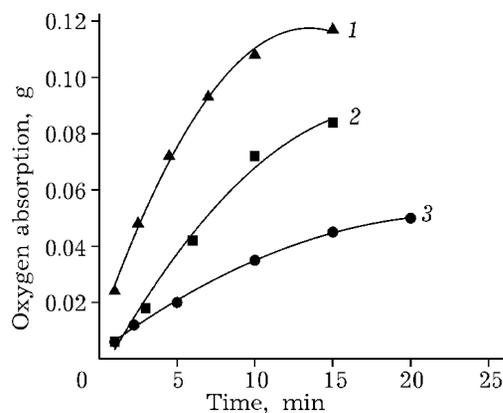


Fig. 5. The kinetics of absorption of molecular oxygen during the oxidation of eugenol by the system: copper oxide (10 g/l) – oxygen (160 °C, 5 g/l eugenol, 0.3 MPa O₂): 1 – 1 M NaOH; 2 – pH 11; 3 – pH 10.

the process under consideration not only directly from eugenol but also from the products of its oligomerization formed during oxidation. The formation of sludgy products at the initial stages of the process is observed by sight; destruction and dissolution of the polymers occur at the subsequent stages. So, both in eugenol and lignin oxidation, vanillin can be formed both from monomeric fragments and directly from the polymeric matrix. Oligomerization can to some extent explain relatively low vanillin yield at 160 °C (molar fraction 38 %) in comparison with the results of oxidation with nitrobenzene (about 90 % [19]). Unlike copper oxide, nitrobenzene is partially soluble in the reaction medium, therefore, it can inhibit radical polymerization more efficiently by oxidizing radicals into quinone methydes; oxidation with oxygen can proceed *via* radical chain mechanism inducing polymerization.

TABLE 1

Composition of the products of oxidation of the lignin model compounds by oxygen in the presence of copper (II) hydroxide

| Initial compound | Concentration, g/l | | [V]/[AV] |
|---------------------|--------------------|--------------------|----------|
| | Vanillin (V) | Acetovanillon (AV) | |
| Guaiacyl propanol-1 | 1.74 | 0.08 | 21.7 |
| Eugenol | 4.14 | 0.05 | 82.8 |
| Guaiacyl ethanol-1 | 0.61 | 0.47 | 1.3 |
| Ferulic acid | 0.03 | 0.01 | 3 |

Note. Oxidation conditions: substrate concentration 5 g/l, copper hydroxide: 1 mole per 3 moles of the substrate; NaOH 60 g/l; oxygen pressure: 0.3 MPa; temperature: 160 °C.

The effect of γ -methyl group on the composition of oxidation products

So, all the kinetic results obtained confirm the proposed mechanism (10)–(14). It differs from the hypotheses described in literature by the participation of γ -methyl group of the propane chain in the formation of vanillin; this difference can be used in planning and performing a discriminating experiment: oxidation of quaiacyl propane and quaiacyl ethane derivatives should result in aromatic oxidation products of different composition. Really, vanillin/acetovanillon ratio for the oxidation of quaiacyl propanol is an order of magnitude higher than that for the oxidation of quaiacyl ethanol (Table 1). Ferulic acid, similarly to quaiacyl ethanol, gives a substantial yield of acetovanillon because the formation of γ -carbonyl structure of (XIV) type is impossible in this case. Such a significant difference in the behaviour of structurally similar substrates in alkaline oxidation shows that the γ -carbon atom of PPU plays a key role in cleaving the α – β C–C bond and thus confirms the proposed mechanism (10)–(15)) and serves against the hypotheses considered above.

Detection of the postulated intermediates of oxidation

The most convincing proof of the mechanism of chemical reactions is detecting the postulated intermediates of the process. For the oxidation of such a complicated substance as lignin, this approach can likely be realized only

TABLE 2

Mass spectra of the intermediate of eugenol oxidation (experiment) and of coniferyl alcohol (database)

| m/e | Peak intensity, % | |
|-------|-------------------|----------|
| | Experiment | Database |
| 180 | 58 | 52 |
| 152 | 21 | 34 |
| 137 | 100 | 100 |
| 124 | 48 | 50 |
| 119 | 17 | 15 |
| 107 | 14 | 12 |
| 103 | 17 | 15 |
| 94 | 15 | 10 |
| 91 | 31 | 41 |
| 77 | 20 | 30 |
| 65 | 12 | 28 |
| 55 | 10 | 23 |

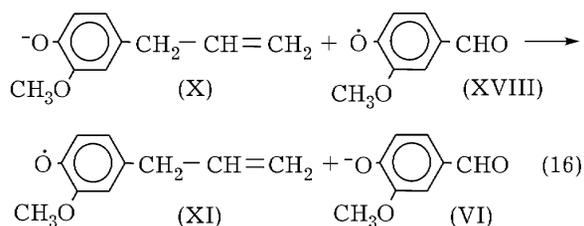
with model compounds. According to the postulated mechanism, relatively stable molecular intermediates of eugenol oxidation should be coniferyl alcohol and aldehyde, which are formed by the addition of hydroxide ion to quinone methide (XII) under thermodynamic control [17, 18].

In fact, coniferyl alcohol is systematically observed by means of GC-MS during the oxidation of eugenol by copper oxide or oxygen in the presence of $\text{Cu}(\text{OH})_2$ at 160–170 °C. The experimental mass spectrum of the substance with molecular mass 180 conventional units and the reference spectrum of *trans*-coniferyl alcohol from the instrument database coincide with high reliability (Table 2, correlation coefficient $\rho = 0.91$), which characterizes the reliability of interpretation of mass spectrum and identification of the substance. Coniferyl alcohol is observed during the oxidation of eugenol within pH range from strongly alkaline to pH 9. Retention time and mass spectra of the coniferyl alcohol detected in the reaction mixture coincide with those of the sample obtained by counter-synthesis according to the procedure described in [31].

Thermodynamic control of the process

An important feature of the mechanism (10)–(15) and many other radical processes of

lignin transformations should be noted: the stages of phenoxy radical interaction with phenolate ion can be rapid and reversible. A similar electron transfer between the semiquinone radicals and hydroquinone anions occurs with a rate close to diffusion [33]. As a result, the concentration ratio of molecular products of oxidation (eugenol, coniferyl alcohol, coniferyl aldehyde, vanillin) can be controlled not only by the kinetics but also by thermodynamics of the corresponding reactions. A substantial role of thermodynamic control is confirmed by the formation of vanillin but not acetovanillone as a main product: hydroxylation of quinone methide (XII) into γ -position is known to be controlled by thermodynamics, while into α -position by the kinetics of the process [18]. To a definite extent, thermodynamic control can be the reason of high selectivity of vanillin formation during the oxidation of eugenols and lignins, that is, relatively low rate of aldehyde oxidation. The authors of [34] observed the oxidation of the syringaldehyde formed in the oxidation of syringic alcohol only after the alcohol conversion degree exceeded 90 %. Single-electron oxidation potential of eugenol, isoeugenol, coniferyl alcohol and other phenols were obtained in [35]; these results indicate that donor substituents decrease and acceptor ones increase the oxidative potential of the compounds. This means that under thermodynamic control vanillin and syringaldehyde are relatively stable products in comparison with eugenols and coniferyl alcohol. The ratio of oxidative potentials of phenoxy radicals formed during the oxidation of the substrate and the product is not less important. It causes a shift of equilibrium thus increasing vanillin yield:



Due to higher potential of phenoxy radical (XVIII) in comparison with the potential of radical formed during one-electron oxidation of eugenol or lignins, equilibrium (16) is shift-

ed to the right. This means that under thermodynamic control the phenoxyl radical (XVIII) acts as an oxidizer of the substrate with vanillin regeneration, if the latter is oxidized into phenoxyl radical in agreement with kinetic regularities.

Chain mechanism of oxidation with oxygen and the process selectivity

The mechanism under consideration (10)–(15) is radical but not chain. Therefore, a decrease in chain length during the oxidation by oxygen should cause an increase in vanillin formation selectivity. The chain length is known to decrease with an increase in initiation rate [36]. Initiation stage for eugenol oxidation with oxygen is electron detachment from phenolate ion (X) by oxygen. From this point of view, an increase in initiation rate due to temperature rise and oxygen pressure increase should lead to the growth of selectivity of eugenol oxidation. Really, a decrease in the process duration to 2–5 min due to an increase in the indicated parameters increases vanillin yield in the catalytic oxidation by oxygen to 80–90 % (molar fraction), that is, to values characteristic of nitrobenzene oxidation (Fig. 6). Such a yield is almost twice as large as that obtained at 160 °C (see Fig. 4) and three times as large as the efficiency of non-catalytic process at 170 °C (see Fig. 3).

In the eugenol and isoeugenol structure, the cleaved α,β C–C bonds are of different nature (single and double, respectively). However, disproportionation of phenoxyl radicals formed

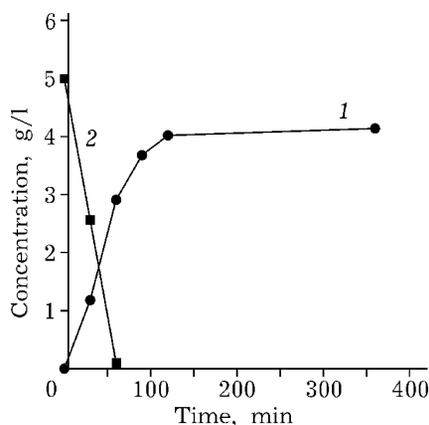


Fig. 6. Curves of vanillin accumulation (1) and substrate consumption (2) for eugenol oxidation by molecular oxygen (170 °C, 10 g/l copper oxide, 5 g/l eugenol, 1.0 MPa O₂, 1 M NaOH).

from both substrates results in the formation of the same quinone methide (XII). From the viewpoint of the mechanism under consideration, and solely from this point of view, this suggests that the selectivity of eugenol oxidation into vanillin should be close to that of isoeugenol. Really, under optimal conditions, oxidation of both substrates by nitrobenzene results in vanillin yield about 90 % [37, 38].

In the first half of the 20th century, eugenol was processed on industrial scale into vanillin by its isomerization into isoeugenol followed by oxidation with nitrobenzene [1]; this process was being patented till the 70ies [39]. Protection of the phenol group was also used for isoeugenol oxidation [1]. From the viewpoint of the mechanism under consideration and the obtained experimental data, neither

TABLE 3

Dependence of the yield of vanillin and syringaldehyde on temperature for non-catalytic oxidation of aspen wood by oxygen in the alkaline medium

| Temperature, °C | Process duration, min | Yield, % of lignin mass | |
|-----------------|-----------------------|-------------------------|----------------|
| | | Vanillin | Syringaldehyde |
| 110* | 40 | 0.7 | 0.8 |
| 170 | 8 | 5.5 | 11.5 |
| 180 | 8 | 7.4 | 15.6 |
| 190 | 5 | 7.8 | 23.4 |
| 200 | 5 | 7.8 | 19.7 |

Note. Process conditions: wood content, 100 g/l; 2 M NaOH; working pressure: 1.7 MPa.

*Catalyst: Cu(OH)₂.

TABLE 4

Selectivity of lignin oxidation depending on the process conditions

| Substrate, catalyst | Temperature, °C | Oxygen pressure, MPa | Process duration, min | Aldehyde yield, % of lignin mass | Ref. |
|------------------------------------|-----------------|----------------------|-----------------------|----------------------------------|------|
| Lignosulphonates, without catalyst | >200 | > 6* | 0.5–5 | 21 | [41] |
| | 160 | 0.05 | 180 | 4 | [2] |
| | 185 | 1.1–1.2* | 70 | 7.4 | [42] |
| Pine wood, copper oxide | 160 | 0.3 | 15–20 | 23 | [15] |
| Pine wood, copper phenanthroline | 170 | – | 180 | 14 | [43] |
| Pine wood, no catalyst | 160 | 0.3 | 15–20 | 12.8 | [15] |
| | 170 | – | 180 | 9.5 | [43] |

*The working pressure for the process is given, that is, the sum of oxygen and water vapour partial pressures.

isomerization nor phenol group protection are necessary for the oxidation of eugenol into vanillin by oxygen. Eugenol isomerization proceeds within several hours in aqueous alkaline medium at 160 °C [1]. Catalytic oxidation of eugenol by oxygen proceeds two orders of magnitude faster than the isomerization: at 170 °C, vanillin yield above 80 % (molar fraction) is achieved within 2–5 min (see Fig. 6); isoeugenol is not detected as intermediate. Hence, eugenol oxidation by oxygen into vanillin proceeds directly according to mechanism (10)–(14) omitting isomerization stage.

The results obtained demonstrate that, in order to increase the selectivity of lignin oxidation into aromatic aldehydes, it is necessary to increase the oxidation rate by making the process conditions more severe. Really, for the oxidation of aspen wood (Table 3) under mild conditions (110 °C, pH 10–12), when the process follows long-chain non-branched route [40], aromatic aldehydes are almost not formed. An increase in the alkalinity of the medium to a 2 M concentration of hydroxide ion (110 °C) transfers the process into the short-chain mode [40], and the total yield of vanillin and syringaldehyde increases to 1.5 % of lignin mass. Temperature rise to 160–200 °C (2 M concentration of hydroxide ions) leads to a sharp increase in the yield of vanillin and syringic aldehyde (see Table 3) till 31 % of lignin mass, which is very close to the best results of catalytic oxidation of aspen wood by oxygen [4]. Optimal oxidation temperature is within the range 180–200 °C, which is much higher than

the temperature typical for the conventional processes involving lignin oxidation into aromatic aldehydes (160–170 °C) [1, 2, 6].

So, for high-temperature non-catalytic oxidation of wood, it is possible to obtain aromatic aldehydes, with vanillin yield up to 7.8 % and syringaldehyde up to 23.4 % of lignin mass. This fact is an indirect confirmation of non-chain character of the mechanism of aromatic aldehyde formation.

The conclusion that severe oxidation conditions are preferable for obtaining aromatic aldehydes is also confirmed by the analysis of literature data (Table 4). Oxidation of lignosulphonates for 5 min and less gives a 3- and 5-times higher vanillin yield in comparison with the oxidation for 1 and 3 h, respectively [2, 41, 42]. A decrease in the duration of pine wood oxidation from 3 h to 20 min causes an increase in aldehyde yield by a factor of 1.5–2 [15, 43].

CONCLUSION

A review of the published hypotheses concerning the mechanism of selective oxidation of lignin into aromatic aldehydes in alkaline medium reveals a number of their shortcomings and contradictions. For example, the known hypotheses are narrowly specific for different oxidants, do not explain the formation of aceto derivatives as by-products, the role of strongly alkaline medium in the process, *etc.* A principal difference of the pro-

posed mechanism from all the known hypotheses is the heterolytic nature of the key stage of retro-aldol cleavage of α,β C–C bond of the phenyl propane structural unit of lignin leading to the formation of vanillin. According to the known hypotheses, the cleavage of this bond occurs *via* homolytic oxidative mechanisms.

The mechanism considered in the present work permits one to solve the above-listed problems. All its stages: the formation of phenoxyl (semiquinone methide) radical (XI), quinone methide (XII), retro-aldol cleavage of the substituted coniferyl aldehyde (XIV) – are well known and are actively used in the field of investigating reactivity of lignin.

The proposed oxidation mechanism is confirmed by a number of experiments; each of them is in fact discriminating:

- coniferyl alcohol is detected as an intermediate of eugenol oxidation process;
- the effect of pH on the kinetics of vanillin formation during the oxidation of vanilidenacetone, eugenol and lignin is of the same character; this confirms the role of retro-aldol cleavage in the investigated processes;
- the composition of aromatic products of the oxidation of guaiacyl propanol and quaiacyl ethanol are principally different, which agrees with the proposed mechanism and cannot be explained with the help of other known hypotheses;
- high rate and selectivity of the catalytic oxidation of eugenol into vanillin by oxygen under severe conditions point to the radical non-chain mechanism of the process.

The proposed mechanism drives us to the conclusion that it is necessary to increase oxidation rate by making the process conditions more severe in order to increase the yield of aromatic aldehydes from lignin. This conclusion is confirmed both by the development of a new method of obtaining aromatic aldehydes from aspen wood [44] and by literature data.

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REFERENCES

- 1 H.V. Mark (Ed.), *Encyclopedia of Chemical Technology*, 2nd Ed., Intersci. Publ., New York, London, 1972, vol. 21, p. 180.
- 2 M. I. Chudakov, *Khimiya lignina*, Lesn. prom-st', Moscow, 1983.
- 3 F. W. Lichtenthaler, *Carbohydrate Research*, 313 (1998) 69.
- 4 V. E. Taraban'ko, N. M. Ivanchenko, N. V. Koropachinskaya, B. N. Kuznetsov, *Chemistry for Sustainable Development*, 4 (1996) 391
- 5 H. Hibbert, *J. Am. Chem. Soc.*, 63 (1941) 3049.
- 6 K. Kurshner, *Zhurn. prikl. khimii*, 28 (1955) 957.
- 7 *Comprehensive Organic Chemistry*, in D. Barton and W. D. Ollis (Eds.), Pergamon press, Oxford etc.; vol. 1: Oxygen compounds, in J. F. Stoddart (Ed.), 1979.
- 8 M. M. Shemyakin, I. A. Red'kin, *Zhurn. obshch. khimii*, 11 (1941) 1142.
- 9 M. I. Ermakova, M. F. Kiryushina, M. Ya. Zarubin, *Khimiya drevesiny*, 5 (1984) 23.
- 10 M. Ragnar, C. T. Lindgren, N. O. Nilvebrant, *J. Wood Chem. Technol.*, 20 (2000) 277.
- 11 J. M. Pepper, B. W. Casselman, J. C. Karapally, *Can. J. Chem.*, 45 (1967) 3009.
- 12 A. F. Gogotov, V. A. Babkin, *Chemistry for Sustainable Development*, 2 (1994) 523.
- 13 A. F. Gogotov, T. I. Makovskaya, V. A. Babkin, *Ibid.*, 4 (1996) 187.
- 14 F. E. Brauns, D. A. Brauns, *Khimiya lignina*, Lesn. prom-st', Moscow, 1964.
- 15 V. E. Tarabanko, N. V. Koropachinskaya, A. V. Kudryashov, B. N. Kuznetsov, *Rus. Chem. Bull.*, 44 (1995) 367.
- 16 *Ligniny. Struktura, svoystva i reaktivnost'*, in K. V. Sarkanen and K. H. Ludvig (Eds.), Lesn. prom-st', Moscow, 1975.
- 17 A. Zanarotti, *J. Org. Chem.*, 50 (1985) 941.
- 18 S. M. Shevchenko, A. G. Apushkinskiy, *Uspekhi khimii*, 61 (1992) 195.
- 19 T. P. Schultz, M. C. Templeton, *Holzforschung*, 40 (1988) 93.
- 20 *The Chemistry of the Nitro and Nitroso Groups*, in H. Feuer (Ed.), John Wiley & Sons, New York etc., 1969, pt. 1.
- 21 J. Gierer, N. O. Nilvebrant, *Holzforschung*, 40 (1986) 107.
- 22 J. Gierer, *Ibid.*, 36 (1982) 55.
- 23 S. Dardelet, P. Froment, N. Lacoste, A. Robert, *Revue A.T.I.P.*, 39 (1985) 267.
- 24 V. E. Taraban'ko, N. A. Fomova, B. N. Kuznetsov *et al.*, *React. Kinet. Catal. Lett.*, 55 (1995) 161.
- 25 V. E. Tarabanko, N. M. Ivanchenko, G. E. Selyutin *et al.*, *Khimiya rastitel'nogo syrya*, 2 (1997) 4.
- 26 V. E. Tarabanko, Ph.D. Thesis, Krasnoyarsk, 1999.
- 27 V. E. Tarabanko, I. I. Il'ina, D. V. Petukhov, E. P. Pervyshina, *Khimiya rastitel'nogo syrya*, 3 (1997) 51.
- 28 V. E. Taraban'ko, Yu. V. Hendogina, D. V. Petukhov, E. P. Pervishina, *React. Kinet. Catal. Lett.*, 69 (2000) 361.
- 29 V. E. Taraban'ko, D. V. Petukhov, B. N. Kuznetsov *et al.*, Sixth European Workshop on Lignocellulosics and Pulping, France, Bordeaux, 2000, p. 621.
- 30 V. E. Tarabanko, S. A. Varganov, D. V. Petukhov *et al.*, *Khimiya rastitel'nogo syrya*, 3 (1998) 101.
- 31 G. F. Zakis, *Sintez model'nykh soyedineniy lignina*, Zinatne, Riga, 1980.

- 32 J. P. Guthrie, K. J. Cooper, J. Cossar *et al.*, *Can. J. Chem.*, 62 (1984) 1441.
- 33 E. T. Denisov, *Konstanty skorosti gomoliticheskikh zhidkofaznykh reaktsiy*, Nauka, Moscow, 1971.
- 34 E. S. Caldwell, C. Steelink, *Biochim. Biophys. Acta*, 184 (1969) 420.
- 35 P. Hapiot, J. Pinson, *J. Phys. Chem.*, 98 (1994) 2641.
- 36 E. T. Denisov, N. I. Mitskevich, V. E. Agabekov, *Mekhanizm zhidkofaznogo okisleniya kislorodsoderzhashchikh soyedineniy*, Nauka i tekhnika, Minsk, 1975.
- 37 V. M. Reznikov, I. V. Sen'ko, *Khimiya drevesiny*, 1 (1968) 51.
- 38 B. Leopold, I. L. Malmstrom, *Acta Chem. Scand.*, 5 (1951) 936.
- 39 Pat. 1802420 Germany, 1970.
- 40 V. E. Taraban'ko, E. P. Pervishina, Yu. V. Hendogina, *React. Kinet. Catal. Lett.*, 72 (2001) 153.
- 41 E. W. Schoefel, US Pat. 2598311, 1952.
- 42 H.-R. Bjørsvik, F. Minisci, *Organic Process Research & Development*, 3 (1999) 330.
- 43 A. F. Gogotov, N. A. Rybal'chenko, V. A. Babkin, *Khimiya rastitel'nogo syrya*, 4 (2001) 39.
- 44 V. E. Tarabanko, E. P. Pervyshina, B. N. Kuznetsov, Pat. 2178405 Ru, 2002.