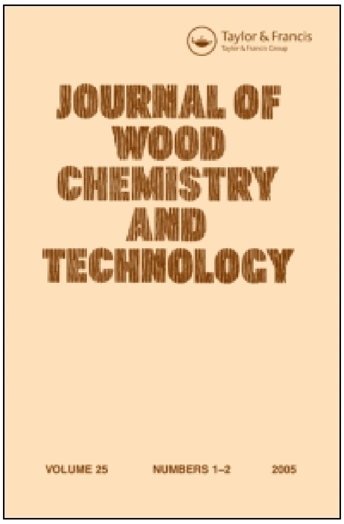

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Oxidative Ammonolysis of Technical Lignins. Part 4. Effects of the Ammonium Hydroxide Concentration and pH

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Oxidative Ammonolysis of Technical Lignins. Part 4. Effects of the Ammonium Hydroxide Concentration and pH

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Abstract: The effects of ammonium hydroxide concentration and pH on the kinetics and reaction mechanism of oxidative ammonolysis of Repap organosolv lignin were studied. The reactions were carried out at 100°C with an oxygen pressure of 8 bar (116 psi) and 0.4–1.6 M [NH_4OH] and 9–12.7 pH. The resulting N-modified lignins were analyzed for elemental composition and methoxyl group content. An increase in ammonium hydroxide concentration increased the rate of nitrogen incorporation, oxygen consumption, CO_2 formation, and lignin dissolution. The rate of nitrogen incorporation was 0.5 order with respect to NH_4OH concentration. The amount of oxygen consumed, oxygen incorporated into the lignin, CO_2 formed, and OMe groups eliminated per mole of nitrogen incorporated decreased with increasing ammonium hydroxide concentration indicating that the increase in [NH_4OH] accelerated nitrogen incorporation more than lignin oxidation. The dependence of the rate of nitrogen incorporation on the reaction pH went through a maximum leading to the

This article is dedicated to the memory of Josef S. Gratzl.

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conclusion that HO^- competes with ammonia in reactions with electrophilic lignin centers resulting in interruption of nitrogen incorporation into the lignin.

Keywords: Technical lignins, oxidative ammonolysis, kinetics of ammonium hydroxide concentration

INTRODUCTION

Oxidative ammonolysis (OA) of technical lignins and lignocellulosics is one of promising ways for utilization of by-products and wastes of the pulp and paper and forest product industries. Since the 1940s, many research groups have been working on the mechanisms of the oxidative ammonolysis.[1–15] The effects of the reaction conditions on the kinetics of the OA is important for understanding the reaction mechanisms. However, comprehensive kinetics studies are very limited.

In our previous studies on the oxidative ammonolysis of REPAP organosolv lignin[12–14] the effects of oxygen pressure and reaction temperature on the kinetics of OA have been studied. In addition, the effect of the reaction conditions on the correlation between nitrogen incorporation and different reaction pathways characterized by oxygen uptake, oxygen consumption, CO_2 formation, and OMe elimination was verified. Oxygen concentration has been shown to directly affect the reaction rate but it does not affect the proportion between different reaction pathways. Oxygen participates directly in the rate-determining step of the overall process of nitrogen incorporation, and does not inhibit the nitrogen incorporation.[13] In contrast, the reaction temperature not only increases the reaction rate but also affects the proportion between competitive reactions of lignin oxidation and nitrogen incorporation.[14] Relatively low values of the activation energy determined could be a result of this competition.

Because ammonium hydroxide is the source of nitrogen in OA of lignin, it is important to study the effect of ammonium hydroxide concentration on the reaction kinetics.

EXPERIMENTAL

Experimental procedures have been described in detail in our previous publications.[12–14] A brief overview follows. Oxidative ammonolysis was conducted in a 300 mL Parr reactor. Lignin (1 g) and 50 mL of NH_4OH solution were placed to the reactor and oxygen was supplied to the reactor at room temperature. The time to temperature (100°C) was 15 min. After the reaction, the reactor was cooled in ice water to room temperature. The reaction mixture was filtered, and the solids were washed with distilled water. A part of the solution was analyzed for CO_2. The remaining solution of soluble lignin was freeze-dried. The soluble and insoluble lignins were then dried in a vacuum oven at 40–45°C to constant mass and weighed. Oxygen uptake and CO_2 formation were determined by the simplified procedure of Deineko and Balin[5] described earlier.[12–14]

To increase the pH of the reaction solution, either 0.1 g (pH 12.7) or 1 g (pH 13.0) of NaOH solution was added to the 0.8 M NH_4OH. To decrease the pH, CO_2 was bubbled through the 0.8 M NH_4OH solution to attain either pH 10 or 9. Analysis of the solutions obtained showed that they contained 6.6 mg/mL and 22 mg/mL of CO_2, respectively in the solution pH 10 and 9 solutions, respectively. In addition, a reaction solution with pH 9 was prepared by addition of 4 mL of acetic acid per 100 mL of 0.8M NH_4OH.

All experiments were run at least twice. The error for the elemental and methoxyl analyses was ±0.1% for a given lignin sample. The average relative error in all analyses was about ±1.5–2%, and the maximum error was approximately 5%. In the determination of O_2-uptake and CO_2-formation, the accuracy of the experiment was lower; the average and maximum error was approximately ±0.1 and ±0.2 mole/C_9-unit, respectively.

RESULTS AND DISCUSSION

The effect of the ammonium hydroxide concentration was studied at 100°C, oxygen pressure of 8 bar, and 3 different concentrations of NH_4OH (0.4 M, 0.8 M, and 1.6 M). As in our previous experiments,[12–14] there were soluble and insoluble lignin fractions, with the amount of the latter decreasing during the oxidative ammonolysis. Nitrogen was incorporated into both fractions. The amount of nitrogen incorporated reported is reported as average (N_a), calculated as previously described:[12–14]

$$N_a(\%) = (N_s L_s + N_i L_i)/(L_s + L_i)$$

where N_s and N_i are the content (%) of nitrogen in the soluble and insoluble *N*-modified lignins, respectively, and L_s and L_i are the yield (g) of soluble and insoluble *N*-modified lignins, respectively.

The maximum percentage of nitrogen in N-lignin (N_∞) was estimated from the experiments at the reaction time of 24 h. This value increased from 14.3% to 17.8% with an increase in the ammonium hydroxide concentration from 0.4 M to 1.6 M (Table 1). The increase in the ammonium hydroxide concentration also increased the rate of nitrogen incorporation (Figure 1). For example, at 165 min reaction, the average percentage of nitrogen increased from 9.60% at 0.4 M to 12.38% at 0.8 M and 14.52% at 1.6 M.

As in our previous experiments, the kinetics of nitrogen incorporation followed pseudo–first order kinetics and had two phases (Figure 1b). The rate of nitrogen incorporation in moles of nitrogen per C_9-unit was estimated by the equation used previously:[14]

$$k = k_N \times N_\infty/(28 \times 100) \times 182, \quad k_N = ln[(N_\infty - N_t)/N_\infty]/t$$

Table 1. Effect of NH_4OH concentration on the kinetics of the oxidative ammonolysis of REPAP organosolv lignin

	Average nitrogen incorporation (N_a)			
		$k \times 10^4$, s^{-1}		Lignin solubilization,
[NH_4OH]	N_∞ (%)	1st Phase	2nd Phase	$k \times 10^4$, s^{-1}
0.4	14.5	1.55	0.572	0.39
0.8	16.1	2.33	0.767	0.48
1.6	17.8	3.05	1.17	0.68

N_∞: Maximum average nitrogen incorporation.

where where N_t is the nitrogen content (%) of a *N*-modified lignin at the reaction time *t*, k_N is the rate constant for nitrogen incorporation, and 182 is a C_9-unit weight of the REPAP organosolv lignin.

Table 1 shows that a twofold increase in the ammonium hydroxide concentration increased the reaction rate in the first phase only 1.4–1.5 times. The reaction rate in the first phase with 1.6 M NH_4OH is approximately 2.6 times that in the second phase. The effect of the ammonium hydroxide concentration on the reaction rate in the second phase is similar to that in the first phase. The reaction rate increases 1.5 and 1.33 times with the increase in the ammonium hydroxide concentration from 0.4 M to 0.8 M and from 0.8 M to 1.6 M, respectively. A fourfold increase in the ammonium hydroxide concentration, from 0.4 to 1.6 M, resulted in an approximately twofold increase in the reaction rate in both phases. Thus, it is likely that the kinetics of nitrogen incorporation is 0.5 order with respect to ammonium hydroxide concentration. Indeed, a plot of log(v) *versus* log ([NH_4OH]) shows a linear correlation with the slope of about 0.5, corresponding to the reaction order with respect to ammonium hydroxide concentration (Figure 2).

An increase in the ammonium hydroxide concentration also increased the rate of lignin dissolution (Table 1, Figure 3). This effect is especially strong on the solubility of original lignin. At 15 min reaction time, that is, just after reaching the reaction temperature, 60% of the lignin was insoluble in 0.4 M NH_4OH, 50% in 0.8 M, and only 32% in 1.6 M solution. The higher solubility of lignin in more concentrated ammonium hydroxide could be caused by the increased pH of the reaction mixture. During the course of OA, the effect of the ammonium hydroxide concentration on the rate of lignin dissolution is not high (Figure 3). Similar to our previous experiments, the kinetics of lignin dissolution follows pseudo–first kinetics through the entire reaction. The reaction rate estimated through the pseudo-first order rate constant (Table 1) increased less than 2 times with an increase of 4 times in the ammonium hydroxide concentration. The plot of log(k) *versus* log ([NH_4OH]) shows the reaction order with respect to ammonium hydroxide

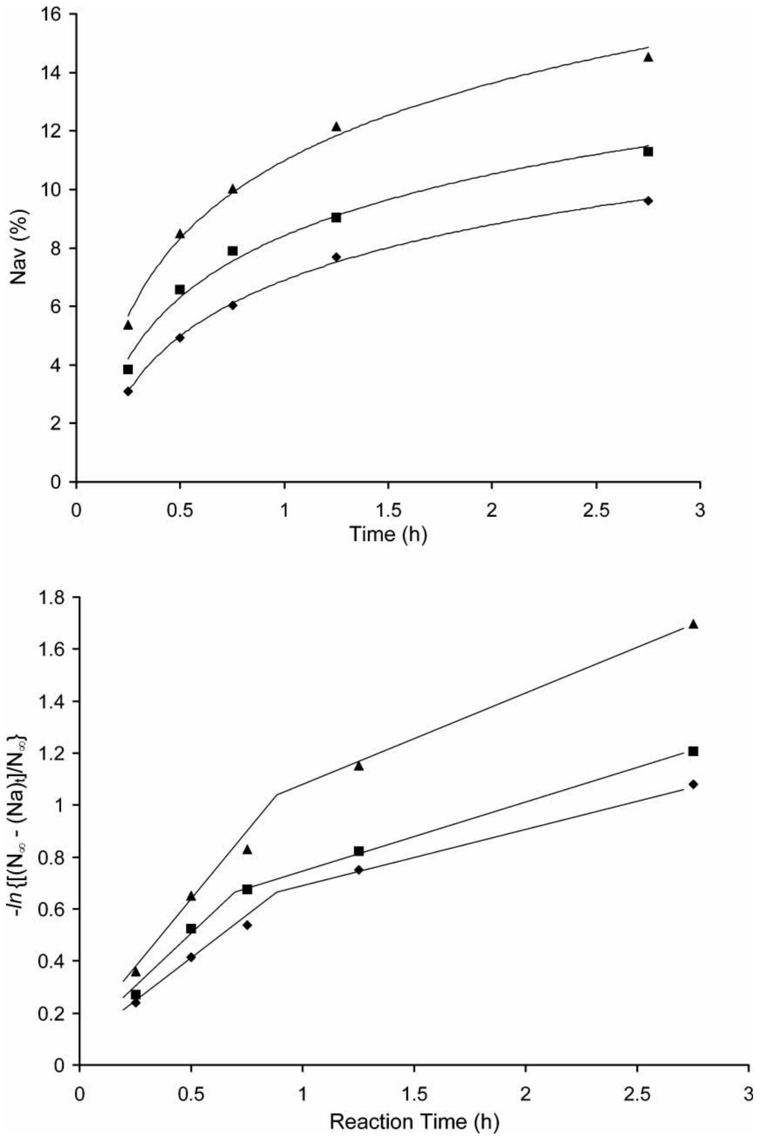

Figure 1. Kinetics of nitrogen incorporation. NH_4OH concentration: ▲–1.6 M, ■–0.8 M, ◆–0.4 M.

concentration is 0.4 (Figure 2). The fractional reaction order is probably due to the fact that the HO^- concentration does not increase directly proportional to the NH_4OH concentration. In addition, nitrogen incorporation into lignin could be followed by reactions of N-condensation of lignin, which result in decrease of its solubility.

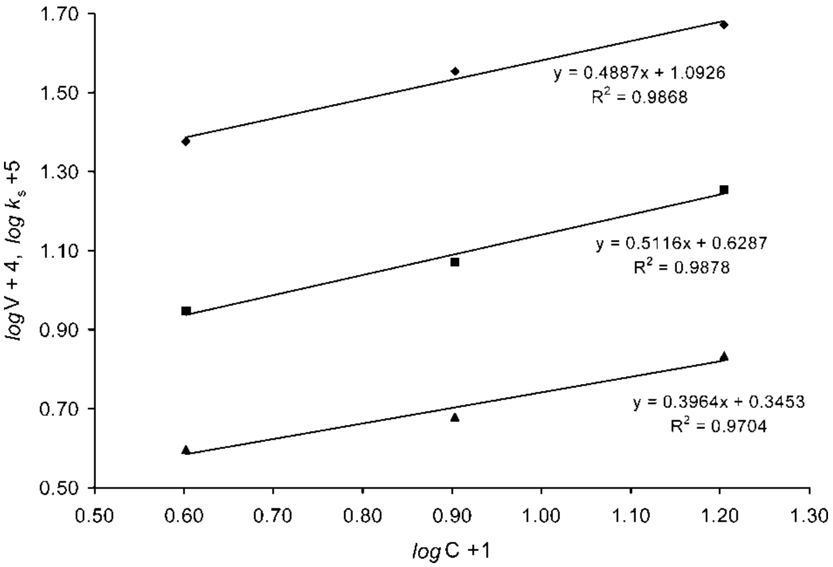

Figure 2. Plot log(v) versus log(c). ◆–nitrogen incorporation in the first phase, ■–nitrogen incorporation in the second phase, ▲–lignin dissolution.

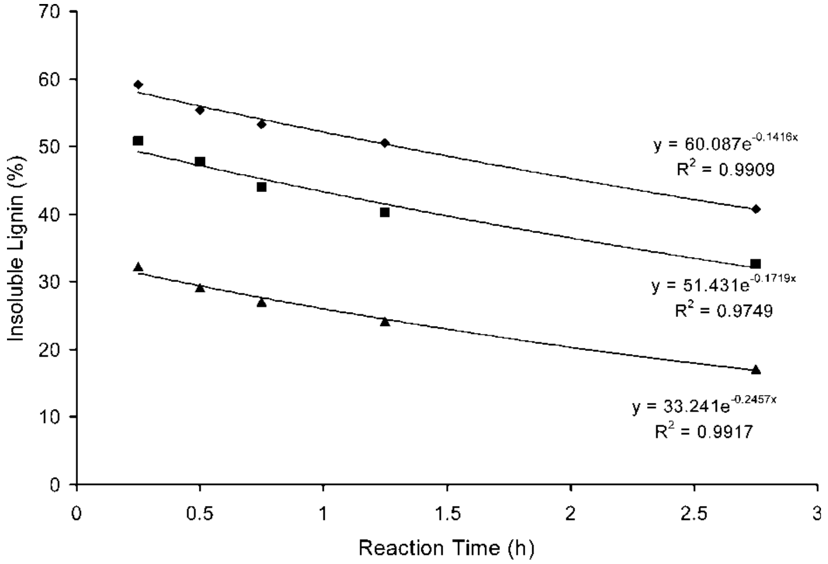

Figure 3. Kinetics of lignin dissolution. NH_4OH concentration: ▲–1.6 M, ■–0.8 M, ◆–0.4 M.

The rate of oxygen uptake increased with an increase in the ammonium hydroxide concentration (Figure 4). For example, at 45 min reaction, an increase in the ammonium hydroxide concentration from 0.4 M to 0.8 M increased the oxygen consumption approximately 1.3 times. Further increasing the ammonium hydroxide concentration to 1.6 M resulted in an increase in the oxygen uptake of approximately 1.2 times. The rate of CO_2 formation noticeably increased when the ammonium hydroxide concentration increased from 0.4 M to 0.8 M (Figure 5). However, a further increase in the NH_4OH concentration to 1.6 M had very little effect on the rate of CO_2 formation.

The amounts of nitrogen incorporated into the lignin (N_{inc}), oxygen incorporated into the lignin (O_{inc}), OMe group elimination, and carbon loss were calculated as follows:

$$N_{inc}(\text{mmole per 1g of original lignin}) = (N_sL_s + N_iL_i)/2.8$$

$$O_{inc}(\text{mmole per 1g of original lignin}) = [(O_sL_s + O_iL_i) - O_{or}L_{or})]/3.2$$

$$CH_3OH(\text{mmole per 1g of original lignin}) = [CH_3O_{or} - (CH_3O_s \times L_s + CH_3O_i \times L_i)]/3.1$$

$$\text{Carbon Loss (mmole)} = [C_{or} - (C_s \times L_s + C_i \times L_i)]/1.2$$

where N_s and N_i are the nitrogen content (%) of the soluble and insoluble *N*-modified lignins, respectively. O_s and O_i are the content (%) of oxygen in the soluble and insoluble *N*-modified lignins, respectively. O_{or} is the content (%) of oxygen in the original REPAP organosolv lignin. CH_3O_{or} is the methoxyl content of the original lignin, CH_3O_s is the methoxyl content of

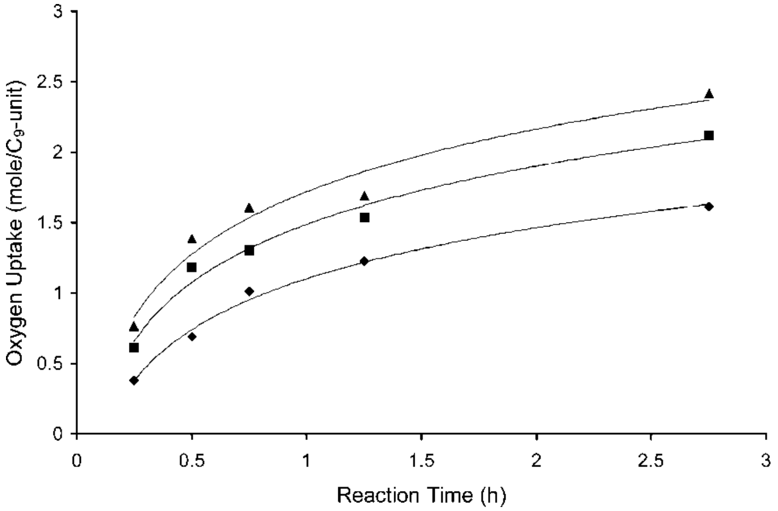

Figure 4. Kinetics of oxygen uptake. NH_4OH concentration: ▲–1.6 M, ■–0.8 M, ◆–0.4 M.

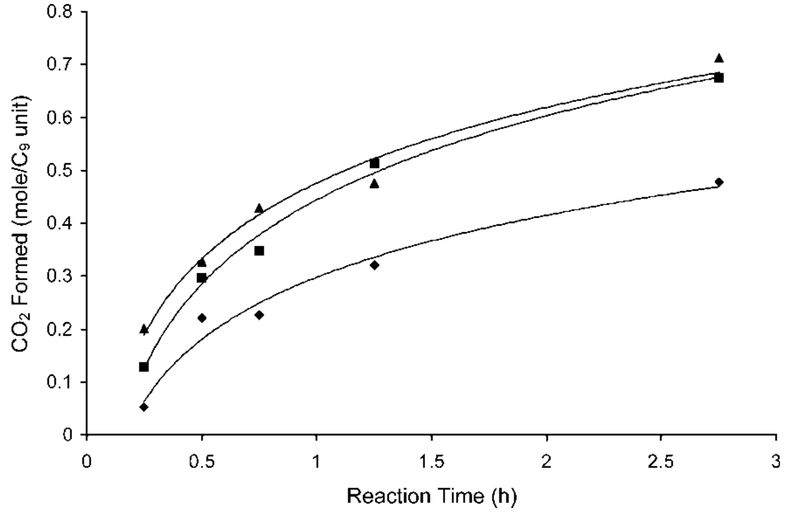

Figure 5. Kinetics of CO_2 formation. NH_4OH concentration: ▲–1.6 M, ■–0.8 M, ◆–0.4 M.

soluble *N*-modified lignins and CH_3O_i is the methoxyl content of insoluble *N*-modified lignins (%), respectively. C_{or} is the carbon content (%) of the original lignin, C_s and C_i are the carbon contents (%) of the soluble and insoluble *N*-modified lignins, respectively. ($L_{or} = 1$ g).

As in our previous experiments, correlations were found between nitrogen incorporation and other parameters of OA through the entire reaction period (Table 2). The results demonstrate that at the same level of N incorporation, lignin oxidation is lower at higher NH_4OH concentration. This is obvious from decreases in the oxygen uptake, oxygen incorporation, CO_2 formation, and OMe group elimination per mole of N incorporated with the increase in

Table 2. Effect of NH_4OH concentration on the moles of carbon and oxygen per mole of nitrogen incorporated in the oxidative ammonolysis of REPAP organosolv lignin

	Loss of carbon (moles)				Oxygen (moles)			
$[NH_4OH]$, M	Total	CO_2	OCH_3	UVOC[a]	Consum	Incorp.	ΔO[b]	In H_2O(as minimum)
0.4	2.53	0.99	1.23	0.31	3.2	0.63	0.96	0.65
0.8	1.96	0.91	—	—	3.2	0.62	—	—
1.6	1.64	0.72	0.57	0.35	2.8	0.57	1.23	0.88

[a] UVOC—unidentified volatile organic compounds.

[b] ΔO = (oxygen consumed) − [(oxygen incorporated) + (oxygen in CO_2) + (oxygen in CH_3O)].

NH_4OH concentration, especially at the NH_4OH concentration of 1.6 M (Table 2). This could be due to higher increase in the rate of nitrogen incorporation than in the rate of lignin oxidation with increase in the ammonia concentration. From a practical point, increase in ammonia concentration results not only in higher reaction rate and final amount of nitrogen incorporated but also in higher yield of the N-lignin at a given percentage of nitrogen due to less degradation of lignin matrix.

Because nitrogen incorporation strongly depends on lignin oxidation and nitrogen is incorporated predominantly into oxidized lignin fragments, the difference in the proportions observed implies that NH_4OH concentration affects the competition between N incorporation and further oxidation of initially formed oxidative intermediates. However, oxygen has been shown to not participate in this competition.[13] Possible species involved in the competition could be HO^- ions. To test this hypothesis, a set of experiments on the effect of pH were performed.

Effect of the Reaction pH on Oxidative Ammonolysis

To study the effect of pH on the reaction rate while maintaining a constant ammonia concentration, the pH of an 0.8 M ammonium hydroxide solution was adjusted with CO_2, acetic acid, or NaOH to the desired level. Carbon dioxide and acetic acid, which generated CO_3^{-2} and CH_3COO^-, respectively, during pH adjustment, were chosen because the pH of the reaction solution decreases in OA due to formation of CO_2 and organic acids, predominantly acetic acid.

Experiments at pH 9 showed that the nature of the resultant anion in pH adjustment appreciably affected the reaction rate (Figures 6–8). The rate of N

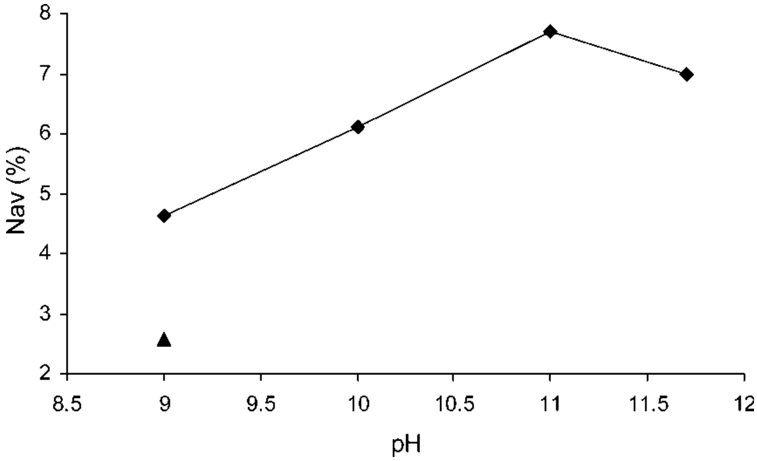

Figure 6. Effect of pH on nitrogen incorporation.

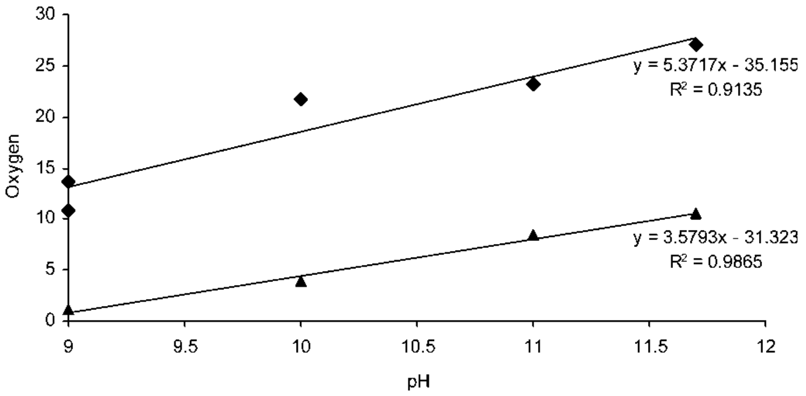

Figure 7. Effect of pH on oxygen consumption (◆) and CO_2 formation (▲).

incorporation and solubilization was higher in the case of CO_2 introduction. This could be due not only to the difference in the nature of the anionic species, but also because a part of the CO_2 escaped into the gas phase with the increase in temperature from ambient to 100°C on reaction start-up. This resulted in an increase in the pH of the reaction mixture leading to an increase in the reaction rate. In support of this hypothesis, the pH after the reaction was higher in this case consistent with part of the CO_2 being transferred into the gas phase. Therefore, more emphasis was given to experiments with the AcOH/NH_4OH system.

The increase in the pH of reaction mixture from 9 to 11 increased the amount of incorporated nitrogen (Figure 6). However, further increase in the pH to 11.7 by addition of NaOH resulted in a decrease in the amount of

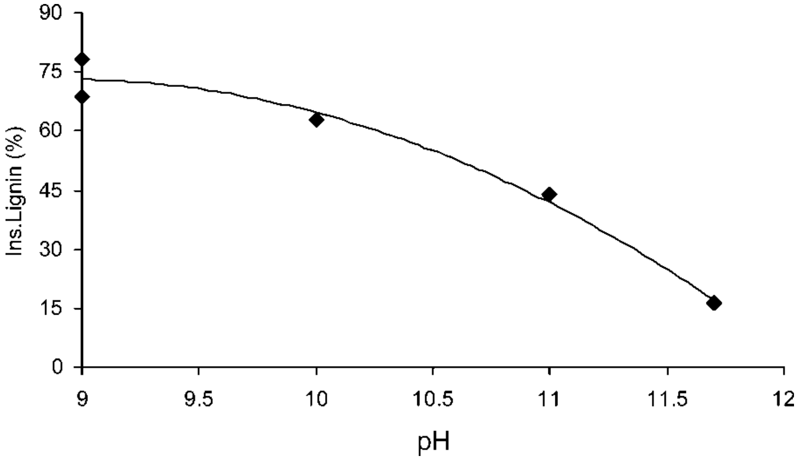

Figure 8. Effect of pH on lignin dissolution.

N incorporated, in contrast to the lignin oxidation. Increase in the reaction pH resulted in increases in the rate of lignin oxidation expressed via lignin solubility (Figure 8), and oxygen uptake and CO_2 formation (Figure 7). The oxygen consumed and CO_2 formed increased linearly with the increase in pH (Figure 7). The effect of pH on lignin solubilization is not linear (Figure 8), probably because an increase in the pH not only increases the rate of lignin degradation but also increases the solubility of the degraded lignin.

Figure 9 shows the effect of pH on the amount of oxygen consumed and incorporated and CO_2 eliminated expressed per 1 mole of nitrogen incorporated. In contrast to the previous plots (Figures 1–8), it reflects the rates of the aforementioned reactions relatively to the rate of nitrogen incorporation (rather than the absolute value) and therefore, it allows estimation of the proportions between various oxidative reactions and the reactions of nitrogen incorporations. It is evident that the proportion of oxidative reactions decreases with a decrease in pH. However, it can be observed that a rather high amount of oxygen is consumed per 1 mole of N incorporated in the solution of $NH_4OH/AcOH$. This requires further investigation.

The Reaction Mechanisms of Oxidative Ammonolysis of Lignin

Possible reaction mechanisms for oxidative ammonolysis of lignins consist of a complex set of consecutive and competitive reactions. Based on our results, the key reaction pathways could be, in general, as presented in Figure 10. The

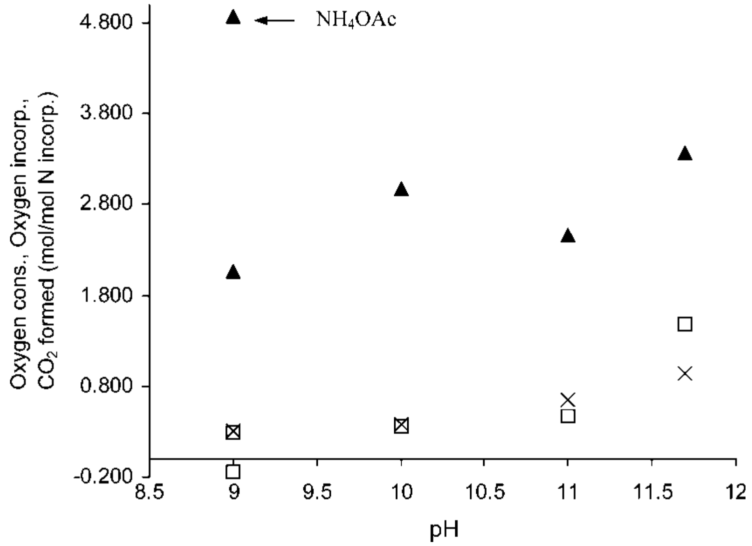

Figure 9. Effect of pH on oxygen mole balance. CO_2 formation (×), oxygen incorporation (□), oxygen consumption (▲).

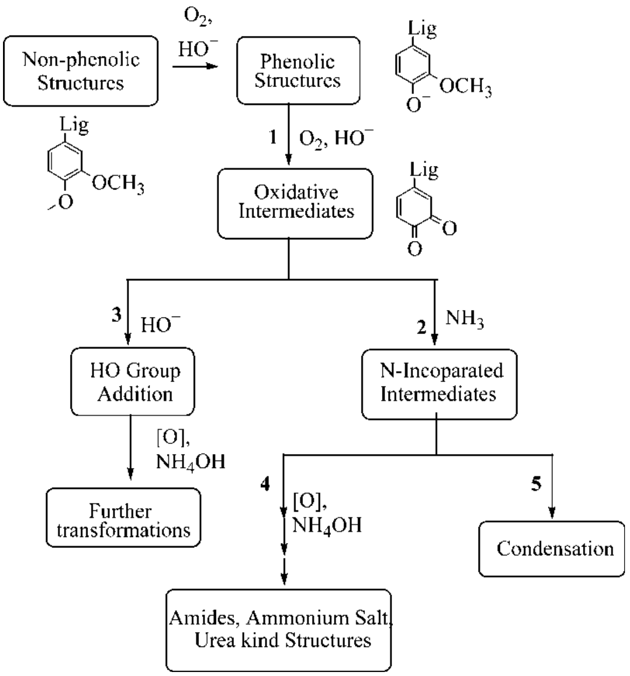

Figure 10. Scheme of the reaction mechanisms in oxidative ammonolysis of lignin.

occurrence of the two phases in the kinetics of nitrogen incorporation implies changes in the reaction pathway and/or in the rate-determining step. The linear correlation between nitrogen incorporation and oxygen uptake, oxygen incorporation, CO_2 formation, and *O*-demethylation through the whole reaction period indicates that the reaction proceeds via the same reaction pathway in the different kinetic phases. This is consistent with NMR and FTIR studies,[12] which show differences only in the intensities of NMR signals and FTIR absorption bands between spectra obtained at different reaction times. This implies that the differences are only quantitative, but not qualitative, confirming the postulation that the reaction pathway does not change during the course of the oxidative ammonolysis. Thus, the different kinetic phases are apparently caused by the change in the rate-determining step, not a changes in the reaction pathway.

The first phase of the oxidative ammonolysis is likely associated with the reactions of phenolic moieties of the original lignin, because their reactivity is much higher than etherified moieties.[16,17] About 60% of the maximum nitrogen uptake being incorporated in the first reaction phase correlates with amount of phenolic hydroxyl groups (70%) in Repap lignin reported by Faix et al.[18] The second phase of the reaction is likely associated with original non-phenolic moieties. The original non-phenolic moieties could participate in the oxidative ammonolysis by their conversion to phenolic moieties via oxidative cleavage of side chains resulting in cleavage of alkyl-O-aryl bonds.[17] This could be the rate-determining step in oxidative ammonolysis of non-phenolic structures, which will determine the oxidation rate of newly formed phenolic moieties, and the corresponding rate of nitrogen incorporation in the second phase.

The correlation between the amounts of nitrogen incorporated into lignin with *O*-demethylation of the lignin, high oxygen uptake, and CO_2 formation suggests that incorporation of nitrogen occurs predominantly after oxidative cleavage of aromatic rings. This is in agreement with intensive degradation of the aromatic rings observed by spectroscopic studies of the corresponding lignins. Accordingly, nitrogen is incorporated into lignin mainly in the form of ammonium salts, amides, and urea type structures but not amines or heterocyclic.[9,15]

The reaction of phenolic moieties most likely starts with oxidation of aromatic rings (Reaction 1, Figure 10). This is one of the rate-determining steps of oxidative ammonolysis because the rate of nitrogen incorporation is directly proportional to oxygen pressure (concentration) in the range of 5–12 bar.[13] Moreover, the first reaction order with respect to oxygen indicates that reactions of oxygen with the substrate do not inhibit nitrogen incorporation. Because the rate of nitrogen incorporation directly correlates with *O*-demethylation, o-quinones are possible key intermediates formed in the initial stage of the oxidative ammonolysis. They can undergo competitive reactions of nucleophilic addition resulting in nitrogen incorporation (Reaction 2) or HO^- addition (Reaction 3). This was clearly indicated by the negative effect of NaOH addition on the nitrogen incorporation (Figure 6). Thus, the role of hydroxide anions (HO^-) in the oxidative ammonolysis is controversial. On the one hand, an increase in pH positively affects the rate of lignin oxidation (and consequently further nitrogen incorporation) due to ionization of phenolic hydroxyl groups. On the other hand, HO^- competes with N-species resulting in a decrease in incorporation of nitrogen into lignin. An increase in NH_4OH concentration increases the concentration of ammonia and HO^-. Therefore, the fractional reaction order with respect to ammonium hydroxide concentration could result from an increase in the reaction rates for nitrogen incorporation and the competitive Reaction 3 with increasing NH_4OH concentration. Overall, however, an increase in the ammonium hydroxide concentration is preferable for nitrogen incorporation (Reaction 2) over HO^- addition (Reaction 3) resulting in higher amount of nitrogen incorporated per OMe group eliminated at higher NH_4OH concentration (Table 2). Similarly, this also leads to lower lignin oxidation (oxygen consumption, CO_2 elimination) per mole of nitrogen incorporated and higher maximal amount of nitrogen incorporated (N_∞) in the experiment with 1.6 M NH_4OH (Tables 1 and 2).

Primary products of nitrogen incorporation (such as imines) undergo further transformations, for example further oxidation with nitrogen incorporation (Reaction 4) and N-condensation (Reaction 5).[4] The relatively low effect of the NH_4OH concentration on the reaction rate could be caused, in addition to those factors discussed earlier, by participation of N-contained species in condensation reactions inhibiting the oxidative ammonolysis of the lignin. The reaction temperature probably affects the ratio between these competitive pathways.[14] The low effective activation energy could be a result of this competition. Radical reactions apparently contribute appreciably to lignin oxidation, whereas the condensation likely occurs via a nucleophilic mechanism. The activation energy of the former is usually higher than that for the latter resulting in preference in lignin oxidation with increasing temperature. This results in more intensive lignin oxidation and higher amount of N_∞ as well as a higher amount of nitrogen incorporated per OMe eliminated and a higher proportion of CO_2 formed per mole of nitrogen incorporated at higher reaction temperatures. Because the oxygen concentration does not affect the ratio between competitive reactions,[13] it is not the oxidant in Reaction 4. Apparently, that could be other oxidants such as hydroperoxy anions (HOO^-) or/and radicals (HOO•), hydroxyl radicals (HO•), or other active oxygen radicals, whose concentrations do not depend on oxygen concentration.

CONCLUSIONS

An increase in the ammonium hydroxide concentration increases the rate of lignin oxidation (oxygen consumption, CO_2 formation, lignin dissolution) and nitrogen incorporation. However, this effect is not linear, and the kinetics of nitrogen incorporation follows a 0.5 order with respect to the NH_4OH concentration implying participation of ammonium hydroxide not only in reaction of nitrogen incorporation, but also in reactions inhibiting nitrogen incorporation.

The effect of the reaction pH on the rate of OA indicates that the role of hydroxide anion is controversial. On the one hand, an increase in pH of the reaction solution increases the rate of lignin oxidation and consequently further nitrogen incorporation. On the other hand, HO^- competes with ammonia resulting in less nitrogen incorporation into lignin.

An increase in the [NH_4OH] accelerates reactions of nitrogen incorporation more than reactions of lignin oxidation The amounts of oxygen consumed, oxygen incorporated into lignin, CO_2 formed, and OMe groups eliminated per mole of nitrogen incorporated decrease with an increase in the ammonium hydroxide concentration.

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