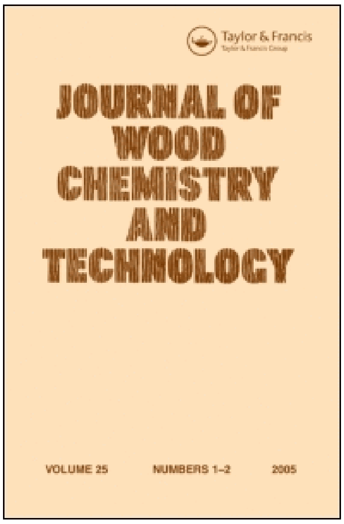

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Demethylation and Nitration of Lignin

Lars Anderssan[a]; Olof Samuelson[a]
[a] Department of Engineering Chemistry, Chalmers University of Technology, Gothenburg, Sweden

To cite this Article Anderssan, Lars and Samuelson, Olof(1985) 'Demethylation and Nitration of Lignin', Journal of Wood Chemistry and Technology, 5: 3, 363 — 378

To link to this Article: DOI: 10.1080/02773818508085199

URL: http://dx.doi.org/10.1080/02773818508085199

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 5(3), 363-378 (1985)

DEMETHYLATION AND NITRATION OF LIGNIN

Lars Andersson and Olof Samuelson,
Department of Engineering Chemistry
Chalmers University of Technology
Gothenburg, Sweden

ABSTRACT

The formation of methanol during treatment of wood meal with nitrogen dioxide is favored by the presence of oxygen and suppressed by addition of sodium sulfate. With 0.5% of added nitrogen dioxide large amounts of methanol were produced at 70°C when kraft lignin was impregnated with 0.5M nitric acid. A markedly increased formation of methanol and nitro groups in the lignin occurred when sodium nitrate was added. At low acidity the effect of sodium nitrate was insignificant. In a solution which was 0.5 molal with respect to nitric acid and 0.8 molal with respect to sodium nitrate, appreciable amounts of methanol and nitro groups were produced even when no nitrogen dioxide was added. This is explained by a generation of nitrogen dioxide from nitric acid in a autocatalytic process favored by high concentrations of nitrate and hydrogen ions.

INTRODUCTION

Treatment of lignin containing materials such as wood pulp with nitrogen dioxide and oxygen gives rise to an oxidation of the lignin, reflected in an improved delignification after a subsequent alkaline stage, and a suppressed depolymerization of the carbohydrates when this stage is an oxygen-alkali treatment [1,2]. The oxidation during the pretreatment and the suppressed depolymerization seem to be closely related to a demethylation of the lignin. It was therefore of interest to study the formation of methanol in more detail. Experiments which comprised

0277-3813/85/0503-0363$3.50/0

determinations of nitro groups were carried out with kraft lignin. Wood meal which offered a more reproducible mass transfer was used in the other experiments.

EXPERIMENTAL

The wood meal from spruce (Picea abies) and birch (Betula verrucosa) had a particle size of 0.5-0.7 mm. Water or aqueous solution was added so that the impregnated wood meal contained 45 g water calculated on 55 g dry wood. If not otherwise stated the charge corresponded to 40 g dry wood. Kraft lignin (Indulin AT from Westwaco Corp.) was after wetting kneaded with Teflon wool (5 g per 1 g of dry lignin) to improve the contact between the lignin and the gas phase during the subsequent treatment.

A 500 ml reactor [1] was evacuated after the introduction of the wood meal or lignin-impregnated Teflon wool. Nitrogen was introduced to atmospheric pressure and the reactor evacuated again. The reactor was then heated to the final temperature in about 20 min and nitrogen dioxide introduced as soon as this temperature was reached. Oxygen was added after 1 min so that atmospheric pressure was approached. The oxygen consumption was less than the added amount. The experiments were interrupted by cooling in tap water and shaking with 200 ml ice-cold water introduced into the reactor to dissolve the methanol present in the gas phase.

The treated wood meal and the lignin were filtered off and the methanol was determined by gas chromatography in the clear solution [3]. litric acid was determined by potentiometric titration with alkali. ppreciable amounts of carboxylic acids were produced in the experiments in which 16-35% of the added nitric acid remained in the reactor. In these experiments pH 3.5 was taken as the equivalent point. After the other treatments more than 95% of the nitric acid was recovered. The formation of carboxylic acids was small and pH 5.0 was chosen as end point.

TABLE 1

Formation of methanol during treatment of spruce meal with 3% nitrogen dioxide at 56°C in oxygen or nitrogen.

Time	Methanol, mmoles per 100 g wood	
min	O_2	N_2
10	7.7	3.6
60	8.3	4.3
120	8.8	4.2
180	9.2	4.1
980	10.9	
1080	11.0	5.0

The lignin was washed carefully with water and air-dried. The moisture and nitrogen contents were determined. During the treatments carbon dioxide, methanol and soluble aromatic compounds were produced. The loss in weight was about the same as the increase in weight due to the introduction of nitrogen containing groups and oxidation of the undissolved lignin. In the calculation of the recovery of nitrogen in the lignin, the yield was taken as 100%. The nitrogen containing groups are mainly nitro groups [4].

The nitrogen contents were determined by means of a CHN-600 Analyzer from LECO Corp. The method is based on combustion in oxygen, removal of oxygen and conversion of the nitrogen oxides to nitrogen by passing the gas over hot copper. The nitrogen contents and the additions of nitrogen dioxide were calculated as percent by weight of dry lignin.

RESULTS AND DISCUSSION

Effect of oxygen

Table 1 shows that the presence of oxygen during treatment of spruce meal with nitrogen dioxide resulted in a markedly increased formation of

TABLE 2

Treatment of spruce meal for 60 min at 56°C in the presence of oxygen.

Oven-dry wood g	Methanol, mmol/100 g after treatment, with 3% NO_2	1% NO_2	HNO_3, % of added NO_2
19.4	8.4	5.4[a]	60[b]
38.8	8.5	5.4	50
54.8	8.7	5.4	50
77.6	9.2	5.4	49

a. In all experiments with 1% NO_2 the wood was impregnated with 0.4 molal nitric acid

b. Percent by mole in the experiments with 3% NO_2.

methanol, compared to that obtained in parallel experiments with nitrogen. No appreciable demethylation of the xylan occurs under the applied conditions which means that the methanol was derived from the lignin. Nitric oxide which is obtained in large proportion when the treatment is carried out under nitrogen is virtually inert [1,5].

The results show that the reoxidation of nitric oxide to nitrogen dioxide contributed substantially to the effect of oxygen during the first 10 min period. Another important reaction is the regeneration of nitrogen dioxide from the nitric acid produced during the treatment. This reaction starts at an early stage of the treatment and continues for a long period of time when the conditions are favorable [6,7]. The formation of methanol after a long duration of the treatment is related to the regeneration of nitrogen dioxide, which is also promoted by oxygen [6]. This explains the effect of oxygen on the methanol formation late in the treatment.

Reactor loading

A change in the composition of the gas phase in the reactor can be achieved instead, by changing the amount of wood meal loaded in the reactor. In the experiments referred to in Table 2, increasing amounts of wood meal of a constant moisture content were introduced into the reactor. In one series of experiments with water-impregnated spruce meal, the addition of nitrogen dioxide was 3%. In a second series the wood was impregnated with nitric acid, and the addition of nitrogen dioxide decreased to 1%.

With water-impregnated pulp the methanol formation increased slightly with increasing reactor loading. The effect was smaller than expected based on determinations of remaining nitrogen dioxide [6,7] which showed that the concentration in the gas phase decreased more slowly at high loading than at low. As indicated by previous investigations and further established by experiments reported below, the nitrogen dioxide in the gas phase promotes the regeneration at least under certain conditions. The low effect on the methanol formation of increased loading of water-impregnated wood, and the negligible effect with wood impregnated with nitric acid are explained by the opposite effect of the decreased concentration of remaining oxygen in the reactor at high loading.

The proportion of the added nitrogen dioxide converted to nitric acid was determined after the treatments of water-impregnated wood meal. As shown in the table this proportion decreased with an increased loading of the reactor. This corroborated the observation that an increased loading led to an enhanced regeneration of nitrogen dioxide.

Sodium sulfate

Treatment of kraft pulp with nitrogen dioxide and oxygen showed that the addition of sodium nitrate resulted in a prominently increased demethylation of the lignin when the solution contained nitric acid of comparatively high concentration. The effect of the sodium nitrate was, however, less than that of the free acid [3]. In a bleach plant with treatment of kraft pulp followed by oxygen bleaching great advantages with regard to the environment are gained by adopting an integrated recovery of the spent liquors. Carry-over of black liquor from the digester and spent liquor from the oxygen bleaching will neutralize the produced nitric acid more or less completely. An addition of mineral acids may,

TABLE 3

Treatment for 60 min at 56°C in the presence of oxygen of wood meal impregnated with sodium sulfate and nitric acid solutions.

NO_2 % on wood	Molality, moles per kg water, of Na_2SO_4	HNO_3	Methanol, mmol/100 g after treatment of Spruce	Birch
3	0	0	8.5	12.1
3	0.2	0	7.1	8.7
1	0	0	2.6	3.7
1	0.2	0	2.1	2.4
1	0	0.4	5.4	6.3
1	0.2	0.4	4.0	5.8

therefore, be necessary to maintain a proper acidity during the treatment with nitrogen dioxide and oxygen. Nitric acid offers great advantages but is more expensive than sulfuric acid unless it can be obtained as a waste product. Sulfuric acid containing sodium sulfate is available as waste acid in many pulp mills. For these reasons, it was of interest to study the effect of additions of sodium sulfate.

Experiments with spruce and birch meal referred to in Table 3 show that sodium sulfate impregnated into the wood meal led to a decreased production of methanol during the pretreatment. This is true both for experiments with and without addition of nitric acid.

In the experiment with 3% nitrogen dioxide, the concentration of the produced nitric acid in the meal was approximately 0.4 moles per kg of water, while with 1% nitrogen dioxide the concentration was approximately 0.1 moles per kg water after treatment without added nitric acid. In the experiments with 0.4M nitric acid impregnated into the wood meal the molality of nitric acid after the treatment was about

0.5 moles per kg of water. Evidently, the added sulfate ions were, in these experiments, and in those with addition of 3% nitrogen dioxide virtually completely converted to hydrogen sulfate ions. This means that in these experiments the addition of sodium sulfate led to a decrease in the concentration of hydrogen ions by approximately 0.2 moles per kg water.

In the experiments with 1% nitrogen dioxide in 0.2 molal sodium sulfate solution without impregnation with nitric acid both hydrogen sulfate and sulfate ions were present in the wood meal during the treatment. Evidently, the concentration of hydrogen ions decreased by more than 50% as a result of the sodium sulfate addition. The decreased formation of methanol resulting from the addition of sodium sulfate can, obviously, be explained by the decreased concentration of hydrogen ions. When comparing the cost of sulfuric acid with that of nitric acid, sulfuric acid cannot be considered as a dibasic acid under conditions of actual interest during treatment with nitrogen dioxide and oxygen.

In the experiments with and without addition of sodium sulfate more methanol was produced from birch than from spruce meal.

Nitric acid

In agreement with results obtained with kraft pulp [3] impregnation of nitric acid into the wood meal before the treatment led to markedly increased formation of methanol during treatment with 1 g of nitrogen dioxide, calculated on 100 g of dry wood (Table 3). To elucidate the influence of nitric acid on the formation of both methanol and nitrogen containing groups, kraft lignin was treated with an exceptionally low addition of nitrogen dioxide (0.5 g corresponding to 10.9 mmol calculated on 100 g dry lignin).

Table 4 shows that significant amounts of methanol were produced even when the lignin was impregnated with pure water before the treatment. The large effect of increased temperature, and the observation that increased duration of the treatment from 60 to 960 min led to an enhanced formation of methanol, indicated that a significant regeneration of nitrogen dioxide occurred under applied conditions. The largest amount of methanol produced from the water impregnated lignin

TABLE 4

Methanol (mmol per 100 g lignin) and nitrogen in lignin after treatment of 7 g kraft lignin in solutions of nitric acid and sodium nitrate. Ratio (by weight) water:lignin 1.5:1.

Temp	Time	Molality of		CH_3OH, mmol		Nitrogen, %	
°C	min	nitrate		0.5%	0.0%	0.5%	0.0%
		H^+	Na^+	NO_2	NO_2	NO_2	NO_2
50	60	0	0	4.2	0	0.01	0
70	60	0	0	7.3	0	0.05	0
70	960	0	0	9.6		0.12	
50	60	0.3	0	8.7	0.8	0.07	0
50	960	0.3	0	9.7	1.6	0.11	0.03
70	60	0.3	0	16.5	4.0	0.14	0.01
70	960	0.3	0	48.8	6.8	0.31	
70	60	0.5	0	27.2	9.3	0.12	0.07
70	60	0	0.8	6.9	0	0.05	0
70	60	0.3	0.4	17.5	3.5	0.12	0.03
70	60	0.3	0.8	18.3	3.3	0.12	0.03
70	60	0.5	0.8	48.6	15.2	0.51	0.13

corresponded to approximately 90 moles per 100 moles of added nitrogen dioxide. The high value obtained despite competing reactions, such as the formation of nitric acid and nitro groups, confirmed that nitrogen dioxide was regenerated. The determinations of nitrogen in the lignin isolated after the treatment showed that after 960 min at 70°C more than 50% of the added nitrogen dioxide was accounted for as nitro groups in the lignin.

Impregnation with 0.3 molal nitric acid instead of water led to a dramatic increase in the formation of both methanol and nitro groups in the lignin. The effect of an increased duration of the treatment at 70°C was much larger than that obtained with water-impregnated lignin. This is consistent with the finding that nitric acid is a source of regenerated nitrogen dioxide [6,8]. The nitrogen content in the lignin after 960 min at 70°C showed that the number of nitro groups was approximately twice that calculated on the assumption that the nitrogen dioxide was converted quantitatively to nitro groups in the lignin. The results confirm that the nitric acid served as a source of regenerated nitrogen dioxide. The formation of methanol in this experiment amounted to 450 moles per 100 moles of added nitrogen dioxide, and 87 moles per 100 moles of added nitrogen dioxide plus nitric acid. Evidently, large amounts of nitrogen dioxide were generated from the nitric acid under these conditions.

As expected from experiments with unbleached kraft pulp [3], an increased molality of the nitric acid from 0.3 to 0.5 moles per kg water gave rise to a markedly enhanced formation of methanol under otherwise unchanged conditions. An extensive demethylation and formation of nitro groups in the lignin occurred in 0.5 molal nitric acid at 70°C even when no nitrogen dioxide was added. The formation of methanol decreased from 27.2 to 9.3 mmoles per 100 g lignin when the addition of 10.9 mmoles of nitrogen dioxide (calculated on the same basis) was omitted. Evidently, added nitrogen dioxide favored the demethylation markedly even when the conditions were such that an appreciable demethylation occurred in experiments without any added nitrogen oxides. These results suggest that, in the presence of lignin, nitrogen dioxide is formed by an autocatalytic decomposition of nitric acid.

Gas analyses showed that large amounts of nitrogen dioxide were produced when 0.5M nitric acid was treated with kraft lignin at elevated temperature in the presence of oxygen. The reaction rate increased after a short induction period the length of which decreased with increasing temperature. In the presence of lignin the decomposition of nitric acid occurred at high rate under such conditions that only a trace amount of nitrogen dioxide was evolved in blanks without addition of lignin. As shown in Table 4, both the formation of methanol and the nitration of the lignin decreased markedly when the molality of the nitric acid was decreased by 40%. When the temperature was lowered to 50°C, the methanol formation was slight and the nitration hardly, significant.

The results strongly indicate that in the experiments without added nitrogen oxides demethylation and formation of nitro groups occurred via nitrogen dioxide produced from the added nitric acid in reactions in which lignin is involved.

Sodium nitrate

During the pretreatment with nitrogen dioxide and oxygen, no effect of sodium nitrate on the formation of methanol was obtained unless nitric acid was present (Table 4). In 0.3M nitric acid the methanol formation increased by approximately 10% when the nitric acid solution was 0.8 molal with respect to sodium nitrate while in 0.5M acid the increase amounted to 80%. Under these conditions sodium nitrate gave rise to a markedly increased nitrogen content in the lignin.

In the parallel blanks without any addition of nitrogen dioxide, the formation of methanol and nitro groups was much lower than in the experiments with 0.5% nitrogen dioxide. Sodium nitrate gave rise to a strongly favored demethylation and nitration when 0.5 molal nitric acid was impregnated into the lignin. At lower acidity the effect of sodium nitrate was small.

The results obtained with and without addition of nitrogen dioxide are consistent with the observation that during pretreatment of kraft pulp[9] with nitrogen dioxide and oxygen, the regeneration of nitrogen dioxide is strongly favored by added sodium nitrate, provided the solution contains hydrogen ions of sufficiently high concentration. A lower threshold concentration has been observed in experiments with kraft pulp indicating that the value depends on the structure of the lignin containing material.

Consumption of nitric acid

In the experiments referred to in Table 5, lignin was heated under oxygen with nitric acid which was 0.85 molal with respect to sodium nitrate. No nitrogen dioxide was added. At 56°C the formation of methanol and nitro groups was very small when the nitric acid concentration was 0.53 moles per kg water. Approximately 95% of the nitric acid was present in the reactor after the treatment. When the molality of the nitric acid was

TABLE 5

Treatment in the presence of oxygen of 9.4 g lignin with aqueous nitric acid containing 0.85 moles of sodium nitrate per kg water. Ratio (by weight) water:lignin 2.95:1.

Temp °C	Time min	Molality of HNO$_3$	CH$_3$OH mmol/ 100 g	N in lignin %	Recovery of N, mole% of added HNO$_3$	
					in lignin	as HNO$_3$
56	30	0.53	1.5	0.04	2	95
56	120	0.53	3.2	0.08	4	95
56	60	1.03	107	2.20	52	25
56	120	1.03	129	2.31	54	22
75	120	0.73	109	1.76	58	16
85	120	0.53	80	1.18	54	22
85	120	0.73	100	1.46	49	22

increased to 1.03, only 22-25% of the nitric acid remained in the reactor. This means that when the concentration of nitric acid surpassed a threshold value at which a rapid reaction was initiated the reaction continued at high rate until the acid concentration was far below this value. This confirms that autocatalytic reactions were involved. Approximately 50% (by mole) of the nitric acid was converted to nitro groups in the lignin. The extensive demethylation of the lignin reflects the prominent generation of nitrogen dioxide in the experiments in which a large proportion of the nitric acid was consumed.

At higher temperature an extensive demethylation and nitration of the lignin was obtained also at an initial nitric acid concentration of 0.53 moles per kg water. After 120 min at 85°C, the molality of the nitric acid remaining in the reactor had decreased to 0.12.

Blowing with oxygen

The treatments of kraft lignin impregnated with nitric acid solutions (Table 4) showed that nitrogen dioxide had a decisive effect, even under such conditions that an extensive demethylation and nitration occurred when no nitrogen dioxide was added. Experiments with kraft lignin were therefore carried out in which oxygen was blown through the reactor during the treatment to decrease the concentration of nitrogen oxides and increase the concentration of oxygen. The preheated oxygen was introduced through a Teflon tubing close to the bottom and removed near the top of the glass flask which served as the reactor. The outlet tube was opened one minute after the addition of oxygen and gas was permitted to leave the reactor through a wash bottle which served as water lock. By this precaution atmospheric pressure was obtained even in the experiments in which large amounts of nitrogen dioxide and other gases were evolved.

In the first experiment in Table 6 the blowing with oxygen was started 10 min after 56°C had been reached and continued until the end of the treatment. A comparison with the results obtained at the same temperature and liquor composition without blowing with oxygen (Table 5) shows that the blowing had a very small effect. The introduction of a small amount of nitrogen dioxide (about 0.7%) before the addition of oxygen led to a modest increase in the nitrogen content in the lignin under the applied conditions, which were favorable for the conversion of the nitric acid to nitro groups via nitrogen dioxide formed as an intermediate.

The fourth experiment was carried out in a smaller reactor with an increased loading. The oxygen flow was the same as in the other experiments, 30 ml per min, determined at room temperature. A decreased nitrogen content in the lignin and a lower proportion of remaining nitric acid were observed. This is explained by a more effective displacement of nitrogen oxides from the reactor than in the other experiments.

A dramatic change occurred when the flow rate was increased to 100 ml per min and the blowing started as soon as the final temperature was reached. As can be seen, only about 1% of the added nitric acid gave rise to nitro groups in the lignin while 96% remained in the reactor as nitric acid after blowing for 60 min. Evidently, the generation of nitrogen oxides was very small in this experiment.

TABLE 6

Oxygen blowing during treatment of lignin with aqueous nitric acid containing 0.85 moles of sodium nitrate per kg water.

Temp °C	Oxygen blowing min	Reactor loading, g Lignin	H_2O	NO_2	Molality of HNO_3	N in lignin %	Recovery of N mole % of added HNO_3 in lignin	as HNO_3
56	10-60	9.4	27.7	0	1.03	2.04	48	26
56	1-60	9.4	27.7	0.07	1.03	2.12	50	27
56	10-60	9.4	27.7	0.07	1.03	2.18	51	29
56[a]	1-60	18.8	55.5	0.14	1.03	1.85	43	17
56	0-60[b]	9.4	27.7	0	1.03	0.05	1	96
75[a]	5-60	0	27.7	0.07	1.03	-	-	104
75[a]	0	9.4	55.5	0	0.52	0.05	1	96
75[a]	5-60	9.4	55.5	0.07	0.52	2.23	52	18
75[a]	5-60	9.4	27.7	0.07	1.03	1.96	46	19
75[a]	5-60	9.4	55.5	0.07	0.33	1.55	57	25
75[a]	1-15	9.4	55.5	0.07	0.52	2.11	49	19
75[a]	1-15	4.7	55.5	0.04	0.52	3.26	38	35
75[a]	0-60[b]	9.4	55.5	0	0.52	0.05	1	96

a. Reactor volume 250 ml. b. Rapid blowing, 100 ml per min.

The first experiment at 75°C listed in Table 6 is a blank in which a solution of 0.85 molal sodium nitrate in 1.03 molal nitric acid was introduced into the reactor which was evacuated and heated to 75°C. When this temperature was reached, a small addition of nitrogen dioxide was made and oxygen introduced so that atmospheric pressure was approached. After 5 min, 30 ml of oxygen per min was passed through the reactor to displace any gases produced during the treatment. After 60 min the treatment was interrupted. The amount of nitric acid in the reactor was larger than the added amount, and virtually equal to that calculated on the assumption that the added nitrogen dioxide was converted to nitric acid. Evidently, the formation of nitrogen oxides directly by decomposition of nitric acid can be disregarded in all experiments with lignin additions reported in this paper.

The second experiment at 75°C was made to study possible reactions during the heating-up period when lignin was present. This period was extended to 30 min while in the other experiments it was about 20 min. When the heating was finished the reactor was cooled and cold water introduced. The recovery of nitric acid was 96%. Only about 1% of the nitric acid was accounted for as nitro groups in the lignin. This shows that only a slight reaction occurred between lignin and nitric acid during the heating-up period.

In three experiments at 75°C shown in Table 6 oxygen was blown through the reactor at the lower flow rate during the period from 5 to 60 min to displace the evolved gases. It is noteworthy that with the same addition (number of moles) of nitric acid a more extensive nitration was obtained with 0.52 molal than with 1.03 molal acid. Similar effects have been observed in other experiments and are ascribed to an extremely rapid evolution of gases during an early period of the treatment at the highest nitric acid concentration. This will lead to a higher pressure and to removal of a larger proportion of gas from the reactor during an initial period of the treatment.

Under applied conditions, a somewhat lower degree of nitration was obtained with 0.33 molal nitric acid. At the end of the treatment only 25% of the nitric acid remained in the reactor, which means that the consumption continued even when the solution was less than 0.1 molal with respect to nitric acid.

In two experiments the treatment at 75°C was interrupted by cooling and blowing with nitrogen after 15 min. Oxygen was blown through the reactor at the lower flow rate during the period 1-15 min. In the experiment with 0.52 molal nitric acid, the nitration and consumption of nitric acid were slightly lower than in the experiment with a fourfold duration of the treatment. The differences were hardly significant. When the addition of lignin was decreased by 50% while the composition and the weight of the solution were unchanged, the nitrogen content in the lignin was much higher than in any of the other experiments. The proportion of remaining nitric acid increased significantly.

The results show that an increased amount of acid nitrate solution relative to that of lignin resulted in an increased nitrogen content in the lignin and an increased proportion of remaining nitric acid. Attempts to suppress the reactions effectively by increasing the oxygen flow under otherwise unchanged conditions were not successful. The results were not reproducible and are not given in the table. The last experiment in the table shows, however, that both the nitration of the lignin, and the consumption of nitric acid decreased strikingly when the addition of nitrogen dioxide was omitted and a rapid stream of oxygen was passed through the reactor as soon as the final temperature was reached. Both the nitrogen content in the lignin and the proportion of remaining acid were virtually the same as in the blank, in which the treatment was interrupted after the heating-up period. Evidently, the continuous displacement of the gas phase suppressed the initiation of the reactions effectively even at 75°C. The results confirm that the formation of nitrogen dioxide during the reaction between lignin and nitric acid is autocatalytic, and is suppressed markedly when the produced nitrogen dioxide is removed effectively.

ACKNOWLEDGEMENTS

The financial support of the 1959 Års Fond för Teknisk och Skoglig Forskning samt Utbildning is gratefully acknowledged.

REFERENCES

1. K. Abrahamsson, L. Löwendahl and O. Samuelson, Sven. Papperstidn. 84, R 152 (1981).

2. O. Samuelson, Pure & Appl. Chem. 55, 695 (1983).

3. T. Engström and O. Samuelson, Tappi 67 (1), 98 (1983).

4. L. Andersson, P. Månsson and O. Samuelson, Sven. Papperstidn. 87, R 59 (1984).

5. B. Bihani and O. Samuelson, Wood Sci. Technol. 18, 295 (1984).

6. O. Samuelson, Proceedings 1983 Intern. Symposium on Wood and Pulping Chemistry, Japanese Techn. Assoc., Pulp and Paper Ind., Tsukuba Science City (1983).

7. T. Engström and O. Samuelson, Sven. Papperstidn. 86, R 173 (1983).

8. T. Engström, O. Samuelson and P. Hall, Wood Chem. Technol. 3, 437 (1983).

9. O. Samuelson and L-A. Sjöberg, Sven. Papperstidn. 87 R 30 (1984).