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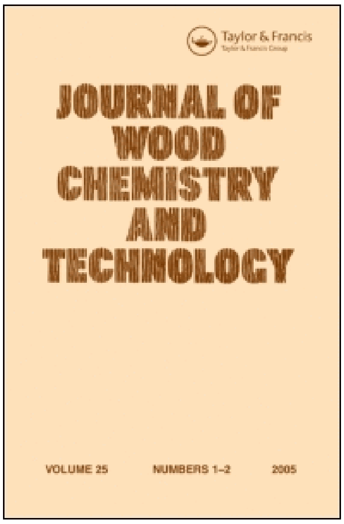

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FORMATION OF NITRIC ACID DURING PRETREATMENT OF KRAFT PULP WITH NITROGEN DIOXIDE AND OXYGEN

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ABSTRACT

During pretreatment of unbleached kraft pulp with 1-4% nitrogen dioxide in the presence of oxygen 50-86 mole percent of the nitrogen dioxide was converted to nitric acid. The conversion was suppressed at high temperature and consistency and by a decreased addition of nitrogen dioxide. In most experiments the proportion of nitric acid decreased with an increased duration of the treatment although nitric acid was produced. The results confirm that nitrogen dioxide is regenerated in a reaction cycle and show that nitric acid serves as a source of nitrogen dioxide.

INTRODUCTION

A major proportion of the nitrogen dioxide consumed during the pretreatment of wood pulp with nitrogen dioxide and oxygen is converted to nitric acid[1]. When no nitrogen dioxide is added dilute nitric acid has virtually no influence on the lignin in the pulp. On the other hand impregnation with nitric acid before or after the pretreatment with nitrogen dioxide and oxygen leads to a greatly improved delignification after a subsequent alkaline stage and to a protection of the carbohydrates when this stage is an oxygen bleaching[2]. This is explained by a regeneration of the nitrogen dioxide in a reaction cycle in which both nitric acid, oxygen and the modified

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lignin participate [3,4]. It was therefore of interest to determine the nitric acid present in the pulp after pretreatment under various conditions.

EXPERIMENTAL

Unbleached kraft pulp from softwood, mainly Scots pine, fully bleached pulp of the same type and purified cotton were subjected to pretreatment in a reactor described previously [1]. If not otherwise stated the experiments were carried out with an unbleached pulp with a kappa number of 39.2. The pretreatment and the sampling were carried out as in a previous study of the formation of methanol[5]. This means that the nitrogen dioxide and nitric oxide present in the reactor after a given reaction time were converted virtually completely to nitric acid. A correction for this formation of nitric acid was obtained by gas analyses carried out separately[6]. The addition of nitrogen dioxide was calculated on the weight of dry pulp.

The nitric acid was determined by an automatic colorimetric method devised by Anderson[7]. The samples were diluted with 0.7 M sodium chloride solution so that the concentration was 5-25 μmol of nitrate per liter. The nitrite concentration amounted to less than 1% of that of nitrate.

To check the possible interference of organic solutes in the spent liquors the determinations of nitric acid in untreated liquors were compared with those in effluents obtained by passing the liquor through columns packed with a non-ionic adsorption resin, Amberlite XAD-2. The deviations amounted to less than ± 2%. After the passage of 5 bed volumes (75 ml) of spent liquor through the column and washing with 2 bed volumes of cold water the colored material adsorbed on the resin was displaced with ethanol. The ethanol was removed by evaporation under vacuum and the residue dissolved in water. The recorded response corresponded to 0.1-0.6% of the addition of nitrogen dioxide during pretreatment of either kraft pulps or wood meal. These results indicate that the applied technique is suitable for determination of nitric acid in the spent liquors without any purification.

RESULTS AND DISCUSSION

Experiments with cotton and bleached kraft pulps impregnated with water to a consistency of 36% showed that during pretreatment with nitrogen dioxide and oxygen the nitrogen dioxide was converted virtually completely to nitric acid after less than 60 min at 56°C.

When unbleached kraft pulps were treated under the same conditions part of the nitrogen dioxide was consumed for nitration of the lignin [1].

Table 1 shows that during pretreatment at 27°C with 4% nitrogen dioxide approximately 85% of the added nitrogen dioxide was converted to nitric acid already after 10 min. Under these conditions only about 1% of the added number of moles of nitrogen dioxide remained as nitrogen dioxide or as nitric oxide which is an important intermediate. Increasing temperature which leads to increased concentrations of nitrogen dioxide and nitric oxide in the gas phase[6] resulted in a decreased conversion of nitrogen dioxide to nitric acid. This decrease was larger than the increased proportion of remaining nitrogen oxides. An increased formation of nitro groups in the lignin related to an improved regeneration of nitrogen dioxide explain this behavior [4]. Very similar results were obtained with kraft pulps from two different mills.

In another series of experiments with 1% nitrogen dioxide and a consistency of 36% the temperature was

TABLE 1

Temperature, NO_2-addition and duration of the pretreatment.

Temp. °C	NO_2 %	Conversion of NO_2 to HNO_3,mole percent, after 10 min	30 min	60 min	120 min
36% consistency, Kappa number 33.5					
27	4	86	85	82	81
56	4	77	75	75	76
70	4	75			
36% consistency, Kappa number 39.2					
27	4	84		80	84
56	4	76	79	79	75
70	4	73	72	68	67
27	2	81	74	75	75
56	2	75	73	74	74
70	2	70	68	67	67
56[a]	2	74	74	70	73
56	1	56	55	55	55
50% consistency, Kappa number 39.2					
56	2	58	59	59	59
56	1	53	55	53	50

a. Displacement of remaining air by nitrogen before addition of NO_2.

increased during the course of the pretreatment. After 10 min at 27°C the conversion of nitrogen dioxide to nitric acid amounted to 60%. The pulp was then heated to 70°C and the treatment continued at this temperature. After 20 min at 70°C the proportion of nitric acid decreased to 54%. This confirms that the nitric acid participates in the reactions which occur during the pretreatment.

A decreased addition of nitrogen dioxide from 2 to 1% led to a significantly decreased proportion of the nitrogen dioxide converted to nitric acid. A decrease was also obtained in most of the comparable experiments when the addition was lowered from 4 to 2%.

In most experiments referred to in Table 1 the proportion of nitric acid decreased when the duration of the treatment was increased. At the higher temperatures 2-4% of the added nitrogen dioxide remained after 10 min. If the nitric acid was instead calculated as a percentage of the consumed nitrogen dioxide the decreased proportion of nitric acid with increasing time is more pronounced than shown in the table. Oxygen and water were present in large excess and nitrogen dioxide at a fairly high concentration especially in the experiments with large additions of nitrogen dioxide at high temperature[6]. It is therefore evident that the production of nitric acid continued at an appreciable rate on prolonged pretreatment. The results confirm that nitric acid participates in the regeneration cycle and serves as a source of regenerated nitrogen dioxide.

The addition of nitrogen dioxide was calculated on the weight of the dry pulp. Since nitric acid is formed by the reaction with water it must be expected that an increased pulp consistency, i.e. a decreased proportion of water should result in a decreased conversion to nitric acid. This was confirmed by the experiments with 2% nitrogen dioxide carried out at 50% consistency included in Table 1 and by the results given in Table 2. The effect of the amount of water in the reactor was, however, fairly small. In most experiments with 1% nitrogen dioxide given in Table 1 the effect of an increase in consistency from 36 to 50% was insignificant. The results show that the kinetics of the formation and decomposition of nitric acid in the presence of unbleached pulp is very complex.

TABLE 2

Influence of the consistency on the conversion (mole percent) of nitrogen dioxide to nitric acid after pretreatment at 56°C for 60 min.

Consistency %	1% NO_2 addition Conversion	1% NO_2 addition Molality	2% NO_2 addition Conversion	2% NO_2 addition Molality	4% NO_2 addition Conversion	4% NO_2 addition Molality
25	61	0.044	78	0.11	80	0.23
34	55	0.062	72	0.16	78	0.35
50	53	0.12	59	0.26	70	0.61

Although a decreased formation of nitric acid with increasing consistency was observed in all experiments reported in Table 2 the molality of the nitric acid in the pulp increased markedly with increasing consistency. This will favor the regeneration of the nitrogen dioxide. On the other hand a high consistency will also result in an increased depolymerization of the carbohydrates by acid hydrolysis.

According to the standard procedure applied in the present work the reactor containing the wet pulp was evacuated before the addition of nitrogen dioxide. Only a small amount of oxygen was therefore present when the nitrogen dioxide was brought into contact with the pulp. To study if the oxygen remaining in the reactor had an influence on the rapid reactions during the short initial period before the introduction of oxygen in excess, experiments were carried out in which the oxygen was displaced by nitrogen and the reactor evacuated again before the addition of nitrogen dioxide. The results included in Table 1 indicate that under applied conditions the influence of the remaining oxygen was small. On the other hand Table 3 shows that the presence of a larger proportion of oxygen in the reactor before

TABLE 3

Influence of the initial partial pressure of oxygen on the percentage of added nitrogen dioxide converted to nitric acid at 56°C and 36% consistency.

Added NO_2, % on pulp	Time min	Conversion, % (by mole) 0 kPa	50 kPa	68 kPa
1	10	61	85	85
1	20	60[a]	64	70
2	10	73	76	78

a. 58% conversion in a separate experiment with nitrogen.

the addition of nitrogen dioxide resulted in an increased conversion to nitric acid. As expected the largest effect was obtained with the lowest addition of nitrogen dioxide and a short duration of the pretreatment. An increased time led to lowered effects. This can be ascribed to the regeneration of nitrogen dioxide in reactions in which the nitric acid was consumed.

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