Institute of Paper Science and Technology
Atlanta, Georgia

IPST TECHNICAL PAPER SERIES

NUMBER 460

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JANUARY 1993

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Submitted to
TAPPI Environmental Conference
March 31, 1993
Boston, Massachusetts

ON THE FORM OF NITROGEN IN WOOD AND ITS FATE DURING KRAFT PULPING

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ABSTRACT

One source of NOx emissions from recovery furnaces is fuel-NOx, which is formed during black liquor combustion by oxidation of the nitrogen contained in black liquors. Previous studies show that the quantity of nitrogen present in wood could fully account for the levels of nitrogen found in Kraft black liquors. Nitrogen containing additives such as brownstock defoamers and evaporator anti-scale agents contribute negligibly to the black liquor nitrogen. Experiments were conducted to test the efficiency of transfer of wood-nitrogen to black liquor during pulping. Three samples of chips, one of Loblolly pine and two of Western hemlock were pulped using a synthetic white liquor under conditions of 30% sulfidity and 25% AA. One of the Western hemlock samples was doped with egg albumin to increase its nitrogen content. Egg albumin was used because of the similarity of the nitrogen compounds in albumin to those found in wood, which are primarily proteins and amino acids. Kjeldahl nitrogen was measured for the chips, the pulp, and the black liquor. Results show that between 70% and 90% of the wood-nitrogen passes directly to the black liquor.

INTRODUCTION

Recently, NOx emissions data from recovery boilers have been summarized and reported (1, 2). The modest temperatures in recovery furnaces suggest that thermal-NOx may not be an important contributor to overall NOx emissions. At the same time, limited data on black liquor nitrogen contents show that all the observed NOx emissions could be accounted for by fuel-NOx (1).

It is known that black liquors contain nitrogen, but little has been published concerning the exact source or the chemical nature of the nitrogen compounds in the black liquor. This information is important because the nature of the source will determine whether or not it is possible to reduce the levels of nitrogen in black liquor prior to firing. The chemical form of nitrogen in black liquor is important because this affects when during the combustion process (and correspondingly where in the furnace) the conversion of fuel nitrogen to fuel NOx could occur.

The purpose for the present paper is to first review the information presently available about the concentration and chemical form of nitrogen in wood and black liquor, then to present the results of experiments intended to determine the efficiency of transfer of nitrogen to black liquor from wood during Kraft pulping.

NITROGEN IN WOOD

Wood invariably contains a certain amount of nitrogen which is essential for the growth and development of the tree. In contrast to herbaceous tissues which typically contain 1-5% nitrogen by weight, woody plant tissues usually contain 0.03-0.10 wt% nitrogen (3). Allison et al. (4) have measured the nitrogen content of a range of tree species. These nitrogen levels, together with other reported wood nitrogen levels (3, 5, 6, 7) are summarized in Table I.

Cowling and Merrill (3) have concluded that hardwoods have a higher weight percent nitrogen than softwoods. The data in Table I do not support this conclusion. Table I indicates that the variation in nitrogen contents among either softwoods or hardwoods is substantially greater than the difference in nitrogen contents between hardwoods and softwoods. The data in Table I for Douglas fir and for European beech also indicate that variations within one kind of tree can also be significant.

Table I. Measured nitrogen levels in wood.

Kind of Wood	*wt% N*	*Ref.*
SOFTWOODS		
Douglas fir	0.051	4
Douglas fir	0.100	7
Loblolly pine	0.068	4
Monterey pine (inner sapwood)	0.090	6
Monterey pine (outer sapwood)	0.148	6
Lodgepole pine	0.071	4
Shortleaf pine	0.130	4
Slash pine	0.050	4
Sugar pine	0.124	4
Western white pine	0.113	4
Longleaf pine	0.038	4
Ponderosa pine	0.052	4
White pine	0.087	4
White fir	0.045	4
Red fir	0.227	4
Red cedar	0.139	4
Engelman spruce	0.118	4
Western larch	0.180	4
Calif. incense cedar	0.097	4
Redwood	0.060	4
Redwood	0.100	7
Cypress	0.057	4
Eastern hemlock	0.106	4
Western Hemlock	0.100	7
Avg.	**0.098**	
HARDWOODS		
Hickory	0.100	4
Chestnut	0.072	4
Black walnut	0.100	4
Red gum	0.057	4
Yellow poplar	0.088	4
White oak	0.104	4
Red oak	0.099	4
Post oak	0.096	4
Black oak	0.070	4
Maple	0.250	7
European beech	0.165	5
European beech	0.090	5
Eucryphia cordifolia	0.058	5
Nothofagus dombeyi	0.042	5
Avg.	**0.099**	

Several investigators (3, 8, 9) have noted that the nitrogen content across the stem generally decreases with distance from the bark. The cambial zone is particularly rich in nitrogen. The cambial zone is the thin layer, a few cells thick, between the inner bark and the sapwood, where cell growth takes place. It contains relatively high concentrations of enzymes, proteins, and other nitrogenous constituents characteristic of living cells. Cowling and Merrill (3) note that the nitrogen content of the cambial zone varies from 1 to 5% by weight and is influenced by a number of factors including individual tree, tree species, and nutritional status. The nitrogen content decreases across the developing xylem such that by the end of the first growing season, the nitrogen content of the wood of most tree species has been reduced to 0.06 to 0.50% by weight. At the sapwood-heartwood interface, the nitrogen content reaches a stable level that in most species is between 0.03 and 0.2 wt% nitrogen. Data collected by Grozdits and Ifju (8) for Eastern hemlock and Madgwick and Frederick (9) for Monterey pine support this description. Grozdits and Ifju (10) used a microtoning technique and determined that the nitrogen content dropped from 2 wt% in the cambial zone to less than 0.7 wt% just 200 μm away from the cambial zone. Since the cambial zone is only a few cells thick (10) the relative amount of nitrogen in the cambial zone will be a negligible contribution to the total nitrogen in the stem.

The fact that sapwood contains more nitrogen than heartwood means that total wood nitrogen content will vary with the relative quantities of sapwood and heartwood. Madgwick and Frederick (9) showed this to be true, by measuring nitrogen concentrations in stemwood of a large number of Monterey pine trees. Nitrogen level was also shown to be lower for larger stem diameters. For the trees studied, a correlation of the data predicted that wood nitrogen content would be 0.064 wt% for a stem of diameter 20 cm and age 15 years, while it would be 0.035 wt% for a stem of diameter 40 cm and age 30 years.

The nitrogen in wood is generally found to be proteinaceous (8). Several studies support this conclusion. Dill et al. (5) found that amino acid nitrogen accounted for 90% of total nitrogen in European beech. Laidlaw and Smith (11) determined that about 70% of the nitrogenous material was protein in the wood of several samples of both sapwood and heartwood of Scots pine. They postulated that the non-proteinaceous nitrogen compounds were present as free-amino acids, ureides, nucleic acids, alkaloids, and inorganic nitrogen. Inorganic nitrogenous constituents of wood were not found to be quantitatively important. When sap samples extracted from a range of plants were examined, nitrate was detected in only about one-third of the species, and in only one or two of these did it constitute more than 1-2 wt% of the total nitrogen (12).

NITROGEN IN BLACK LIQUOR

Only limited study has been made of the nitrogen in Kraft black liquors due both to the low concentrations of nitrogen and its insignificant impact on pulping. Measurements of total nitrogen contents in liquors have been reported (1). Expressed as a weight percentage of the dry liquor solids, nitrogen levels are in the range 0.05-0.24 wt% with the average being 0.11 wt%. Niemelä (13) studied low molecular weight compounds in birch Kraft black liquor using mass spectroscopy and found three heterocyclic nitrogen compounds, but did not report their concentrations.

Lignin is a major component of Kraft black liquors and some information is available on the chemical form of nitrogen compounds in lignin. Dill et al. (5) made Kjeldahl nitrogen determinations of the nitrogen contents in the Klason lignins of four hardwood species. Comparison of total nitrogen in one of the hardwood lignins to results from amino acid analysis showed clearly that the nitrogen content of the lignin was almost exclusively amino acid nitrogen. Fukuda et al. (14) determined that the nitrogen content in lignin from loblolly pine originated from protein amino acids. In both of these lignin studies a wide range of amino acids were found.

The average values for nitrogen in wood from Table I are 0.098 wt% for softwoods and 0.099 wt% for hardwoods. Assuming a fiber yield of 45%, and a value of 1.5 for weight ratio of black liquor solids to unbleached pulp, and assuming all of the wood nitrogen to be present in the liquor would give a black liquor nitrogen content of 0.15 wt%. This value is greater than the average value of 0.11 wt% reported previously for black liquor nitrogen, suggesting that the nitrogen in wood could account for all the nitrogen present in black liquors.

The wood-nitrogen could be retained by the pulp during pulping. However, Kjeldahl nitrogen analysis of samples of unbleached pulp from two Kraft mills pulping softwoods showed nitrogen contents of less than 0.015 and 0.018 wt%. Using the 45% yield value, and the average softwood nitrogen content of 0.098 wt% (from Table I), this represents less than one-tenth of the wood nitrogen, indicating that only a small fraction of wood nitrogen partitions with the pulp. This partitioning of wood-nitrogen between pulp and black liquor during pulping is the subject of the experiments presented below.

NITROGEN CONTAINING ADDITIVES

A certain amount of nitrogen could potentially enter the black liquor stream by way of process additives such as brownstock defoamers and evaporator anti-scale agents. However, the magnitude of contributions from these sources to black liquor nitrogen is small. A typical oil-based brownstock defoamer consists of a carrier oil with dispersed filler particles which are the active foam breaking agents (15). The particles are hydrophobic and are usually wax and/or silica. A common wax used is ethylenebistearamide ($C_{38}H_{76}N_2O_2$) or EBS (16). Typical EBS levels are 2-5 wt% of the defoamer, and defoamer addition rates are typically 0.5 kg defoamer/tonne of product. Assuming 3 kg defoamer/tonne of product with 5 wt% EBS in the defoamer, and assuming all of the EBS nitrogen partitions to the black liquor, would give 0.007 kg of nitrogen/tonne of product, or about 0.0005 wt% nitrogen in the black liquor.

Scale inhibitors are added directly to the evaporators to prevent metal ions from depositing on the evaporator tubes and causing decreases in evaporator efficiency. Scale inhibitors may contain aminophosphanates and are added at levels of approximately 0.25 kg/tonne of product. At this relatively low addition rate, nitrogen contributions to black liquor from scale inhibitors would be even smaller than the contribution from nitrogen in defoamers.

EXPERIMENTAL PROCEDURES AND RESULTS

Wood chips were obtained from two different tree samples, a Loblolly pine and a Western hemlock. Nitrogen levels in these samples were determined by Kjeldahl analyses. The Western hemlock chips were then divided into two parts for use both neat and with nitrogen doping. Each chip sample was subjected to laboratory Kraft pulping cooks using a synthetic white liquor consisting of a solution of Na_2S and NaOH with a sulfidity of 30%. All batches used a 4:1 liquor-to-wood ratio and a 25% AA. Digestion temperature profiles were 100°C to 170°C in 90 minutes and then constant 170°C for an additional 90 minutes yielding an H-factor of approximately 1700. One of the Western hemlock cooks was conducted after adding egg albumin to the cook in order to raise the nitrogen levels. Egg albumin was used as a nitrogen source because it is a water-soluble protein containing approximately 13.25 wt% nitrogen. The nitrogen in egg albumin exists as proteinaceous amine groups similar to wood protein. Egg albumin was added to the level of 0.89 wt% of the oven dry chip solids.

After each cook, the digester was blown and weak black liquor was separated from the chips using a centrifuge. Chips were then disintegrated and washed. The pulp samples were analyzed for Kjeldahl nitrogen content, kappa number and viscosity. The kappa number, viscosity, estimated pulp yield, and resulting black liquor mass for each cook are shown in Table II.

Table II. Analysis of pulp samples.

	Loblolly Pine	Western Hemlock	Doped Western Hemlock
Kappa number	18	15	18
Viscosity	12.8	7.7	12.0
Yield, %	45	43	44
BL mass/wood mass	0.76	0.78	0.77

Kjeldahl nitrogen content was also determined for the weak black liquor. The weak black liquor was then evaporated under vacuum in a rotovap apparatus in order to concentrate the black liquor to approximately 62% solids. Kjeldahl nitrogen content of the concentrated black liquor was then measured. The analysis of the black liquors is shown in Table III. The Kjeldahl nitrogen contents for each sample are shown in Table IV.

Table III. Analysis of the black liquor samples.

Composition, % oven dry basis	Loblolly Pine	Western Hemlock	Doped Western Hemlock
Carbon	35.4	34.0	36.1
Hydrogen	3.65	3.87	3.43
Oxygen	33.8	33.3	33.2
Sodium	19.9	20.1	19.3
Sulfur	4.87	4.74	3.90
Potassium	0.66	0.79	1.03
Carbonate-carbon	0.24	0.14	0.29
Sulfide-sulfur	1.73	1.31	0.42
SO_3-sulfur	1.20	1.16	0.59
Thiosulfate-sulfur	2.27	2.49	2.67
Sulfate-sulfur	0.15	0.18	0.21

Table IV. Kjeldahl nitrogen contents of the wood chips, pulp, weak black liquor, and concentrated black liquor.

Kjeldahl nitrogen, ppm OD basis	Loblolly Pine	Western Hemlock	Doped Western Hemlock
Wood chips	500	410	410
Doped chips	–	–	1599
Washed pulp	124	122	181
Weak BL	520	520	1420
Concentrated BL	590	270	1250

The information in Tables II and IV can be combined to give a material balance on the nitrogen entering the digester. Table V shows the percent for wood-nitrogen (or doped wood-nitrogen) that was found in the pulp and in the weak black liquor.

Table V. Nitrogen in pulp and in weak black liquor as a percent of the original wood-nitrogen.

	Loblolly Pine	Western Hemlock	Doped Western Hemlock
Washed pulp	11%	13%	5%
Weak BL	79%	99%	68%
Total	90%	112%	73%

Shown in Table VI is the percent of the nitrogen in the weak black liquor found in the concentrated black liquor.

Table VI. Nitrogen in concentrated black liquor as a percent of that in weak black liquor.

	Loblolly Pine	Western Hemlock	Doped Western Hemlock
Concentrated BL	113%	52%	88%

DISCUSSION

Examination of Tables V and VI show that the current procedures do not lend themselves to complete and highly accurate nitrogen balances. Low values of total nitrogen accounting in Table V could be due to losses during the blow or during washing. However, the high value could only be due to experimental error in nitrogen determination of the wood chips or black liquor. Table VI reveals the same limitation for the current data. The exceptionally low value for the comparison of nitrogen in the concentrated black liquor for the undoped Western hemlock case also indicates unanticipated experimental errors. Despite these limitations, the data seem clear on the partitioning of nitrogen between pulp and black liquor. For these fairly harsh Kraft cooking conditions, a very large fraction of the nitrogen in the original wood will be found in the black liquor as opposed to the pulp. Further, the run using egg albumin to increase the proteinaceous nitrogen content of the cook indicates that Kraft cooking conditions will favor amine nitrogen transfer to the black liquor.

CONCLUSIONS

The literature on the form of nitrogen in wood indicates that most nitrogen is in the form of proteins or amino acids. The nitrogen is concentrated in the active growing layer of the tree. This will favor higher wood nitrogen in smaller trees and in individual trees near the top where the tree is narrower.

For the limited tests carried out here under fairly harsh Kraft pulping conditions, the nitrogen contained in the wood chips transferred primarily to the black liquor rather than the pulp. This preferential transfer occurred also when the wood was doped with egg albumin which contains nitrogen in amine groups similar to wood. Further tests need to be carried out to improve the accuracy and reliability of the experimental procedure, and to examine the specific impact of different pulping conditions on nitrogen partitioning during pulping.

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ACKNOWLEDGEMENTS

The authors acknowledge the support of the Institute of Paper Science and Technology and its member companies. We would also like to thank Don Sachs and Blair Carter for their work in carrying out the pulping experiments.