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ON THE SOURCE AND CHEMICAL FORM OF NITROGEN IN KRAFT BLACK LIQUORS

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ABSTRACT

It has been suggested that an important source of NO_x emissions from recovery furnaces is fuel NO_x , which is formed by oxidation of nitrogen contained in black liquors. Regarding the sources of this black liquor nitrogen, a review of previous studies on nitrogen in wood coupled with material balances shows that the quantity of nitrogen present in wood can fully account for the levels of nitrogen found in kraft black liquors. Nitrogen-containing additives such as brownstock defoamers and evaporator antiscaling agents are expected to contribute negligibly to the black liquor nitrogen. Generally, the nitrogen content of wood is highest in young and developing tissue, and decreases with both increasing distance from the bark and increasing age. Very little data exist on the specific nature of nitrogen compounds present in black liquor. Based on existing knowledge of the nitrogen compounds in wood and lignin, it is hypothesized that the chemical form of nitrogen-containing compounds in black liquors is primarily that of wood proteins and amino acids.

KEYWORDS

nitrogen oxides, fuel nitrogen, black liquor, recovery furnace, fuel NO_x , amino acids, protein

INTRODUCTION

Recently, NO_x emissions from recovery furnaces have received additional attention in the pulp and paper industry, in part, due to the practice of higher solids firing. Recovery furnace emission data have been summarized and reported (1,2) showing that NO_x concentrations in flue gases increase as black liquor solids concentrations increase. These increases, however, are modest when compared to the magnitude of increase expected based on published thermal NO_x rate information. It has been suggested (1) that this discrepancy between theoretical and observed trends is because fuel NO_x constitutes a majority of the total recovery furnace NO_x . Fuel NO_x results from the oxidation of nitrogen compounds which are present in black liquor. The formation of fuel NO_x is less sensitive to temperature increases than is thermal NO_x .

It is known that black liquors contain nitrogen; however, little is known 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 feasible to reduce the levels of nitrogen in black liquor prior to being fired. The chemical form is important because this affects when during the combustion process (and correspondingly where in the furnace) the conversion of fuel nitrogen to fuel NO_x will occur.

The purpose for this paper is to review the information presently available about the chemical form of black liquor nitrogen, and to utilize wood composition data and material balance considerations in examining the probable sources of black liquor nitrogen. It is intended that the material provided will ultimately aid in understanding possibilities for controlling recovery boiler NO_x emissions.

NITROGEN IN BLACK LIQUOR

Very little study has been made of the nitrogen in kraft black liquors. This is not surprising considering that nitrogen is present in small amounts in black liquor and has thus been of little significance in the technical aspects of chemical 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 with the average being 0.11. Niemelä (3) studied low molecular

weight compounds in birch kraft black liquor and, using mass spectroscopy, found three heterocyclic nitrogen compounds. Unfortunately, the concentrations of these compounds in the black liquor were not reported. To our knowledge, no other studies have been made to directly determine the chemical form of nitrogen-containing compounds in black liquors.

A limited amount of information is available on the chemical form of nitrogen compounds in lignin. This is of interest because lignin is a major component of kraft black liquors. Dill et al. (4) made Kjeldahl nitrogen determinations of the nitrogen contents in the Klason lignins of four hardwood species. Total nitrogen levels were 0.1-0.4 wt/wt% of dry solids. Considering that lignin represents about 30% of kraft black liquor solids, these lignin nitrogen levels are consistent with black liquor nitrogen levels. 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. (5) 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 (most of the common amino acids) was found.

NITROGEN IN WOOD

Wood invariably contains a certain amount of nitrogen which is essential for the growth and development of the tree. In contrast with herbaceous tissues which typically contain 1-5% nitrogen by weight, woody plant tissues usually contain 0.03-0.10% nitrogen (6). Allison et al. (7) have measured the nitrogen content of a range of tree species. These nitrogen levels, together with other reported wood nitrogen levels (4,6,8,9), are summarized in Table I.

The average values from Table I are 0.098% for softwoods and 0.099% for hardwoods. Using these averages, and an overall material balance, it is seen that wood contains enough nitrogen to account for the nitrogen in black liquors. 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%. This value is greater than the average value of 0.11% reported previously for black liquor nitrogen,

showing that there is more than enough nitrogen in wood to account for the nitrogen present in black liquors.

The material balance also suggests that the majority of the wood nitrogen partitions during the pulping process with the black liquor stream. This hypothesis was further supported by making measurements of the nitrogen contents of two pulps. Samples of unbleached pulp were obtained from two kraft mills which were pulping softwoods. Kjeldahl nitrogen analyses of these pulps showed nitrogen contents of less than 0.015 and 0.018% by weight (dry basis). Using a 45% yield value and the average softwood nitrogen content of 0.098% (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.

Cowling and Merrill (6) have concluded that hardwoods have a higher weight percent nitrogen than softwoods. The data in Table I do not confirm this. These data indicate that the variation in nitrogen contents among softwoods (or among hardwoods) is substantially greater than the difference in nitrogen contents between hardwoods and softwoods. As noted in Table I for Douglas fir and for European beech, variations within one kind of tree can also be significant.

NITROGEN DISTRIBUTION ACROSS STEM

It has been noted by various investigators (6,10,11) 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 (6) 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. The nitrogen content continues to decrease gradually from the first annual increment across the sapwood. At the sapwood-heartwood interface, the

nitrogen content reaches a stable level that in most species is between 0.03 and 0.2% nitrogen.

Hypotheses have been presented (6) to explain the radial gradients in nitrogen content by considering the life of a tree in four phases. These are dilution, elution, parenchyma death, and stable phases. In the dilution phase, a finite amount of nitrogen exists in the developing xylem, but its weight percent is diluted by successive depositions of cellulose, lignin, and other secondary cell wall substances. The dilution phase continues until the process of lignification is complete. During the elution phase, the lignified xylem transports soluble nitrogen compounds away to nourish the living tissues in the stem and crown of the tree. The parenchyma death phase occurs after the current annual growth increment as more and more of the parenchyma cells die and lose their cytoplasm coinciding with a general decrease in nitrogen content across the sapwood. Finally, stable nitrogen levels are observed in the heartwood.

Data collected by Grozdits and Ifju (10) for Eastern hemlock and Madgwick and Frederick (11) for Monterey pine support the phases hypothesized by Cowling and Merrill (6). These data showed the same trend of decreasing nitrogen content at locations farther from the tree bark. Much of the gradient occurred within a very narrow region immediately adjacent to the cambial zone. Grozdits and Ifju (10) used a microtoning technique and determined that nitrogen content dropped from 2% in the cambial zone to less than 0.7% just 200 μm away from the cambial zone. Since the cambial zone is only a few cells thick (12), 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 (11) showed this to be true by measuring nitrogen concentrations in the stemwood of a large number of Monterey pine trees. Four- and 8-year-old trees showed higher nitrogen levels than 17-, 22- and 29-year-old trees. The 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 weight% for a stem of diameter 20 cm and age 15 years, while it would be 0.035 weight% for a stem of diameter 40 cm and age 30 years.

Although this specific correlation applies only to the particular wood samples studied, the form of the correlation indicates general trends which could be expected for all trees. One expects higher average nitrogen content in stemwood that is closer to the crown of the tree where diameter is smaller and heartwood content is less compared with stemwood closer to the base of the tree. One also expects that wood from limbs will have higher average nitrogen content than wood from the tree stem only.

CHEMICAL FORM OF NITROGEN IN WOOD

The nitrogen in wood is generally considered to be proteinaceous (10). Several studies support this conclusion. Dill et al. (4) found that amino acid nitrogen accounted for 90% of total nitrogen in European beech. Laidlaw and Smith (13) 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 nonproteinaceous nitrogen compounds were present as free-amino acids, ureides, nucleic acids, alkaloids, and inorganic nitrogen. It would seem that inorganic nitrogenous constituents of wood are not 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 (14).

NITROGEN-CONTAINING ADDITIVES

A certain amount of nitrogen can potentially enter the black liquor stream by way of process additives such as brownstock defoamers and evaporator antiscaling agents. It is worthwhile to consider the potential magnitude of contributions from these sources to black liquor nitrogen.

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 1-6 lb defoamer/ton of product. Assuming 6 lb defoamer/ton of product with 5 wt% EBS in the defoamer,

and assuming all of the EBS nitrogen partitions to the black liquor would give 0.014 lb of nitrogen/ton of product, or about 0.0005 wt% nitrogen in the black liquor. This value is insignificant when compared to the average black liquor solids nitrogen level of 0.11 wt%, and shows that nitrogen in defoamer additives is not likely an important source of black liquor nitrogen.

Evaporator scale inhibitors may contain aminophosphonates and are added at levels of approximately 0.5 lb/ton of product. Scale inhibitors containing nitrogen would be directly fired to the recovery boiler and contribute to the nitrogen in black liquor. However, 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.

DISCUSSION

Considering that wood contains enough nitrogen to account for the nitrogen in black liquors, and that the dominant form of nitrogen compounds in wood is proteins and amino acids, it seems reasonable to hypothesize that the primary chemical form of nitrogen-containing compounds in black liquor is that of wood proteins and amino acids. Since amino acids and chains of amino acids are primarily nonheterocyclic, this suggests that a minority of nitrogen in black liquors is bound in heterocyclic rings. With only a few exceptions, the nitrogen in proteins and amino acids is bound as primary amides (N bonded to carboxyl C) and primary and secondary amines.

The radial distribution of nitrogen concentration in stemwood may be an important consideration for recovery furnace operation. Increases in wood nitrogen concentration will result from pulping younger or smaller diameter trees. With the present state of knowledge in the area, it seems likely that increases in wood nitrogen will yield increases in black liquor nitrogen and in recovery furnace NO_x emissions. If this is true, then it is expected that pulping of younger and/or smaller diameter trees will result in higher NO_x emissions from the recovery furnace.

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I. Measured nitrogen levels in wood.

SOFTWOODS		
<u>kind of wood</u>	<u>wt/wt% N</u>	<u>Ref.</u>
Douglas fir	0.051	7
Douglas fir	0.100	9
Loblolly pine	0.068	7
Monterey pine (inner sapwood)	0.090	8
Monterey pine (outer sapwood)	0.148	8
Lodgepole pine	0.071	7
Shortleaf pine	0.130	7
Slash pine	0.050	7
Sugar pine	0.124	7
Western white pine	0.113	7
Longleaf pine	0.038	7
Ponderosa pine	0.052	7
White pine	0.087	7
White fir	0.045	7
Red fir	0.227	7
Red cedar	0.139	7
Engelman spruce	0.118	7
Western larch	0.180	7
Calif. incense cedar	0.097	7
Redwood	0.060	7
Redwood	0.100	9
Cypress	0.057	7
Eastern hemlock	0.106	7
Western Hemlock	<u>0.100</u>	9
Avg.	0.098	
HARDWOODS		
Hickory	0.100	7
Chestnut	0.072	7
Black walnut	0.100	7
Red gum	0.057	7
Yellow poplar	0.088	7
White oak	0.104	7
Red oak	0.099	7
Post oak	0.096	7
Black oak	0.070	7
Maple	0.250	9
European beech	0.165	4
European beech	0.090	4
Eucryphia cordifolia	0.058	4
Nothofagus dombeyi	<u>0.042</u>	4
Avg.	0.099	