

EFFLUENT FROM RADIO FREQUENCY/VACUUM DRYING OF SOFTWOODS: CHARACTERIZATION AND TREATMENT

Robert L. Zwick
Heatwave Drying Systems
Castlegar, B.C.

Paul A. Bicho
PAPRICAN
Vancouver, B.C.

Stavros Avramidis, Tao Chen, Collette Breuil, John N. Saddler
University of B.C.
Vancouver, B.C.

Introduction

In recent years, volatile organic chemicals (VOCs) have become of critical concern to many forest products operations. This is because VOCs have been suspected as major causes of respiratory problems to humans and also as toxic compounds to fish and animals. Furthermore, they are also suspected to contribute to the ozone depletion phenomenon.

VOCs naturally exist in wood and are usually carried out from the wood pores by the free water when it flows and evaporates from the surface of a piece of lumber during kiln, dehumidification, superheated steam/vacuum and radio frequency/vacuum drying.

Radio frequency vacuum (RF/V) drying has been shown to be an efficient and economical means of drying softwood lumber (Avramidis and Zwick 1992, Zwick and Avramidis 1993). An added advantage of RF/V kiln drying is that VOC emissions are substantially reduced because kiln design and operation stipulate that vapors generated during drying are condensed and collected (Avramidis and Zwick 1992). In contrast, VOCs are released into the atmosphere during conventional heat-and-vent lumber drying and may adversely affect the air quality of the localized environment (Walling 1975).

Preliminary unpublished studies showed that condensates generated during RF/V kiln drying of wood were found to have a biological oxygen demand (BOD₅) as well as being acutely toxic towards rainbow trout resulting in LC₅₀ values of 8% (vol/vol) and lower. Therefore these condensates were recognized as having a potentially detrimental effect on receiving waters, if discharged without prior treatment. Conventional biological sewage treatment was considered an adequate means of condensate disposal for mills located near an existing facility. However, in many instances, kilns may be situated in remote regions that are not serviced by such facilities and therefore would require on-site condensate remediation. Such a

treatment should not only reduce BOD₅ and detoxify condensates but also be compatible with the flows and production schedules typical of a lumber drying mill.

Wastewater discharge permits for British Columbia require that effluents for discharge into receiving waters meet strict guidelines. These include BOD₅ levels less than 50 mgL⁻¹, total suspended solids (TSS) levels less than 60 mgL⁻¹, pH of 6.5-8.5 and no mortality of a test species of fish (rainbow trout) after 96 hours of exposure to full strength (100%) effluent. The objective of this study was to characterize the condensates generated during the RF/V drying of three softwood species and to identify physic-chemical treatment strategies that could generate an effluent that meets discharge requirements.

Material and Methods

Condensate preparation and storage

Green lumber pieces (100mm X 100mm X 2240mm) of Douglas-fir (DF), western red cedar (WRC) and western hemlock (WH) were obtained from a B.C. sawmill. All lumber was a mixture of heartwood and sapwood and was exposed to air during transportation and handling (~2 hr). The length of time uncut logs were stored in the mill yard was not determined. The lumber samples were considered to be typical of the total sample that was kiln dried. Nine samples of DF and WH were stacked and dried in a laboratory scale RF/V kiln as previously described (Avramidis et al. 1994, Liu et al. 1994). The WRC was prepared in a similar fashion except that only 2 samples were dried. The vapors generated were condensed, collected and used in this study. Lumber dried in the RF/V kiln were not treated with any antisapstain chemicals prior to drying. Condensates were stored in amber bottles at 4°C and periodically re-examined for pH, COD and toxicity. No changes in these parameters were noted in any of the condensates over the course of this study.

Condensate treatment

pH adjustment: Condensates were adjusted to pH 7 with 2 molar NaOH or 2 molar HCl as required.

Filtration: Condensates were filtered under vacuum through Whatman 934-AH glass microfiber filters (average particle retention diameter of 1.5 µm).

Hydrogen peroxide (H₂O₂) oxidation: Chemical oxidation, which has been used in the amelioration of some types of waste waters, was examined as a means of improving effluent quality in this study (Carey 1992, Vella and Munder 1993, Wang and Chen 1992). Condensates were chemically oxidized by the addition of 15 g of H₂O₂ and 1.5 mg of FeCl₃ per L (final concentration) and allowed to react at room temperature for 2 hours with occasional mixing. After this time period, excess H₂O₂ was quenched by the addition of Na₂S₂O₃.

Adsorbent treatment: The removal of organic materials by selective adsorption to solid matrices is a well established water treatment strategy. Several adsorbents were evaluated for their ability to treat RF/V condensates. These included Amberlite IRA-400 OH (strong anion exchanger) and Amberlite IR-118H (strong cation

exchanger), Amberlite XAD-4, Kaolin clay (Carter and Hyder 1993) and technical grade activated charcoal.

All adsorbents were washed with deionized water prior to use. Individual adsorbents (50 ml) were packed into 60 ml polypropylene syringes that had been lined with Whatman 934-AH glass microfiber filters. Condensates were gravity fed through the packed columns at flow rates of 0.25-0.5 bed volumes per min. Volumes of 200-500 ml of condensates were passed through each column before adsorbent regeneration was required. Regeneration was as instructed by suppliers. Kaolin clay and activated charcoal adsorbents were not regenerated but discarded after use.

Condensate analysis

Treated and untreated condensates were analyzed for chemical oxygen demand (COD - closed reflux method), biological oxygen demand (BOD₅), total suspended solids (TSS) and pH according to standard methods (APHA 1985). Bacterial seed for the BOD₅ assay was obtained from Polyseed (Polybac; Bethlehem, PA). Titratable acidity was determined by following the pH of a condensate while specified volumes of 0.1 N NaOH were added. The titratable acidity is reported as the grams of NaOH required to neutralize 1 L of condensate to pH 7. Carbohydrates were determined by the phenol/sulphuric acid test (Chaplin 1986).

Acute toxicity towards *Daphnia magna* (Environment Canada 1990) and the luminescent *Photobacterium phosphoreum* (Microtox) (Environment Canada 1992) were determined according to established protocols. With the former assay, the condensate concentration required to kill 50% of the *Daphnia magna* test organisms within 48-hrs (i.e. LC₅₀) were determined from log plots of % mortality vs. condensate concentration (% vol./vol.). For the Microtox assay, the condensate concentration required to inhibit 50% of the bacterial luminescence (i.e. EC₅₀) after 5 min exposure times was determined from plots of gamma vs. condensate concentration, where gamma is a corrected measure of light loss as described by Environment Canada (1992) protocols. The EC₅₀ was that condensate concentration, expressed as % vol./vol., that gave a gamma value of 1. Toxicity is inversely proportional to either LC₅₀ or EC₅₀. The highest condensate concentrations that could be tested using the Microtox and *Daphnia magna* assays were 50% and 100%, respectively.

In all cases effluent pH was neutralized prior to toxicity assays. Controls of distilled water that had been subjected to treatments were not toxic to either *Daphnia magna* or *Photobacterium phosphoreum*, nor was Na₂S₂O₃, when added to quench excess H₂O₂, found to be toxic at the concentrations used (~10 mgL⁻¹). The EC₅₀ values reported for the Microtox assay are an average of duplicate readings. However, the LC₅₀ values for the *Daphnia magna* assay are from one determination. Repeated evaluation of untreated condensates, in triplicate, by both bioassays, gave coefficients of variance between 20-25%. This was considered standard for both bioassays.

Further chemical characterizations included resin and fatty acid analysis as determined by the modified method of Voss and Rapsomatiotis (1985). Acetate concentrations were determined by high performance liquid chromatography (HPLC)

using a Waters 625 LC system equipped with an HPX87H column (Biorad), which was kept at 45°C and eluted with 0.005 M H₂SO₄ at a flow of 0.4 ml min⁻¹. Detection was by refractive index (Waters 410 Differential Refractometer). Acetate quantification was by the external standard method.

Results and Discussion

Characterization of three condensates

All condensates were evaluated for BOD₅, COD, pH and acute toxicity. They were also analyzed for several compounds that were thought likely to be present and of environmental concern (Table 1). The ratios of the condensate volumes generated to that of the wood that was dried were 33 Lm⁻³, 138 Lm⁻³ and 180 Lm⁻³ for the DF, WH and WRC, respectively. These values are 10-90% lower than those reported previously (Avramidis and Zwick, 1992) and reflect differences in the moisture content of the woods as well as kiln drying schedules.

TABLE 1. Characterization of RFV condensates from three softwoods

	Douglas-fir	Western Hemlock	Western Red Cedar
Wood Volume Dried (m ³)	0.21	0.21	0.05
Condensate Volume (L)	7	29	9
pH	4.9	5.6	4.9
Titrateable acidity (mg NaOH L ⁻¹)	160	150	260
Acetate (mgL ⁻¹)	805	251	167
COD in mgL ⁻¹ (+/- std)	1456 (33)	585 (36)	873 (88)
BOD ₅ in mgL ⁻¹ (+/- std)	224 (45)	110 (27)	155 (50)
Carbohydrate	ND*	ND*	ND*
Resin acids	<0.5 ppm	<0.5 ppm	<0.5 ppm
Microtox - EC ₅₀ (+/- std.)	2.3% (0.5)	2.8% (0.6)	1.7% (0.4)
<i>Daphnia magna</i> - LC ₅₀ (+/- std)	9% (1)	27% (4)	25% (3)

* Not Detected

Condensates had a pale yellow to orange color and were acidic in nature. The low pH values and relatively high titrateable acidities indicated that much of the organic material was acidic (Table 1). The TSS contents of the three condensates were less than 5 mgL⁻¹ and not of environmental concern. However, BOD₅ levels ranged from 110-224 mgL⁻¹ and were considered unacceptable for a wastewater discharge permit in British Columbia. Condensates from commercial scale RFV kiln drying have reported BOD₅ levels ranging from 500-1000 mgL⁻¹. Variations in BOD₅

are thought to be due to differences in moisture content of the woods and process operations. Chemical oxygen demand levels were 5-6 fold higher than the corresponding BOD₅, suggesting that some of the organic compounds in the condensate may be either toxic to bacteria or biologically recalcitrant. This would suggest that the biological treatment of these condensates alone would require long residence times, a distinctive microbial population or other specific conditions for condensate detoxification.

All three condensates contained acetate which accounted for 59%, 44% and 20% of the COD from the DF, WH and WRC condensates, respectively (60 mg of acetate = 64 mg of COD). The remaining COD was considered to be other extractives released during drying. Acetate, which is readily degraded by many bacteria, accounted for most of the BOD₅ in the WRC condensate. This suggested that other organic compounds present in the condensate were not inhibitory to the bacteria used in the BOD₅ assay. However, the measured BOD₅ levels of the DF and WH condensates were lower than expected from the acetate concentrations. This suggested that the biological seed used in the BOD₅ assay was inhibited by other compounds present in these condensates. Cytotoxicity towards bacteria has been demonstrated in other studies with distillates from several wood species, including DF, that are similar to the RF/V condensates (Singer et al. 1995). Acetate was also the main buffering agent in the condensates. No carbohydrates, resin or fatty acids were detected in any of the condensates suggesting that non-volatile compounds did not contribute to either the BOD₅ or toxicity of RF/V kiln waste waters.

The condensates were found to be acutely toxic towards *Photobacterium phosphoreum* (Microtox) with EC₅₀ levels of the three condensates ranging between 1.7-2.8%. This assay has been recognized as a useful indicator of relative toxicity in pulp mill effluents (Fein et al. 1994, Firth and Beckman 1990) and was used as a such in this study. However, it should be emphasized that Microtox is not a substitute for fish toxicity assays and results obtained with the bacterial assay are only indicators of potential toxicity to some aquatic life forms (Fein et al. 1994). Condensate LC₅₀ values towards *Daphnia magna* ranged between 9 and 27%. This is comparable with similar findings that showed RF/V condensates were acutely toxic towards rainbow trout with LC₅₀ values between 2-8%. Condensates were neutralized prior to Microtox and *Daphnia magna* assays, therefore toxicity was not attributable to the acidic pH. Neutralization is a standard treatment option with many acidic waste waters. Also, as the original samples had not been treated with antiseptics prior to RF/V kiln drying, condensate toxicity was not considered to be of anthropogenic origin, but due rather to natural wood components. Therefore, condensate components originating from the dried woods are toxic towards *Daphnia magna* and both *Photobacterium phosphoreum* and the mixed bacterial culture used in the BOD₅ assay. These results are comparable to other studies which also have shown that condensates from woods are toxic and mutagenic towards bacteria (Singer et al. 1995).

Screening of options for the treatment RF/V condensates

Several treatment strategies were evaluated for their ability to neutralize, detoxify and reduce condensate COD or BOD₅. Preliminary studies with the DF condensate found that an orange brown precipitate developed after neutralization. Although filtration removed this precipitate, the filtrate was still toxic and BOD₅

removal was only 11% (Table 2). Similar results were obtained with the WH and WRC condensates. Pollutant destruction by chemical oxidation or pollutant removal by specific adsorbents were evaluated as means of condensate treatment. To expedite the evaluation of the various treatments only pH, COD and Microtox values of treated and untreated condensates were compared (Figures 1 and 2).

TABLE 2. Effects of neutralization and filtration on the pH, COD and toxicity of a Douglas-fir condensate from a commercial scale kiln.

	A	B
Final pH	3.6	7.0
BOD ₅ (mgL ⁻¹)	1922	1711
Microtox - EC ₅₀	1.2%	0.7%
<i>D. magna</i> - LC ₅₀	17%	17%

A: Before neutralization and filtration

B: After neutralization and filtration

Charcoal was ineffective in reducing the COD concentration of the three condensates and was not examined further. Although Kaolin clay removed 95% of the WRC condensate COD, it was much less effective with the other two condensates and detoxification was relatively minor. Similar results were noted with the cation exchange resin. In comparison, 40-80% of the COD of all wastewater was removed by the XAD and anion exchange resins. There was also significant detoxification with these adsorbents. Although anion exchange was expected to remove most of the acetate and other organic acids that contribute to COD and toxicity, only the WH condensate was completely detoxified by this treatment. Therefore, some of the toxicants present in the WRC and DF condensates must be neutral. The XAD resin was very effective in detoxifying all three condensates confirming that toxicants in the condensates are hydrophobic. However, acetate, which is a major component of the COD, is relatively hydrophilic and was not removed. This is evident by the high COD remaining after XAD treatment. Although significant improvements in condensate water quality were obtained with anion exchange and XAD adsorbents, residual COD and toxicities were still unacceptable, indicating that other treatments should be explored.

Oxidizing agents have been used to treat several types of waste water's including pulp mill effluents (Carey 1992; Liu et al. 1994; Voss and Rapsomatiotis 1985). However, pulp mills typically generate 20-100 m³ of effluent per day, which makes this an expensive treatment option. In comparison, a commercial RF/V kiln generates 2-4 m³ per day (Avramidis and Zwick, 1992) and chemical oxidation may be feasible. Hydrogen peroxide (H₂O₂) was selected as the oxidizing agent. This oxidant has many benefits; it is commercially available; it degrades to H₂O; residual H₂O₂ can be easily quenched; H₂O₂ is most effective under acidic conditions (pH 3-5) typical of RF/V condensates and; H₂O₂ plus catalytic amounts of Fe²⁺/Fe³⁺ form a strong oxidizing agent (Fenton's reagent) (Vella and Munder, 1993).

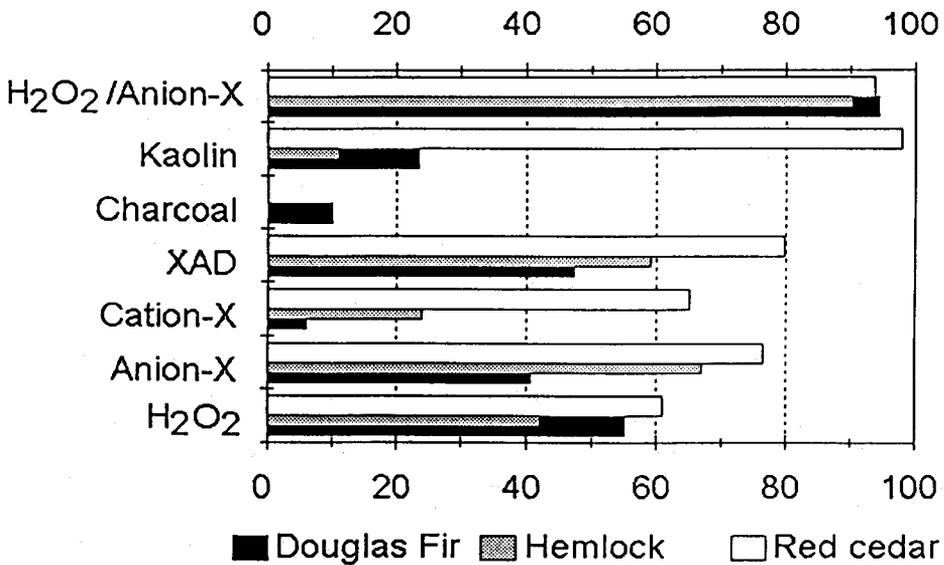


FIGURE 1. COD removal.

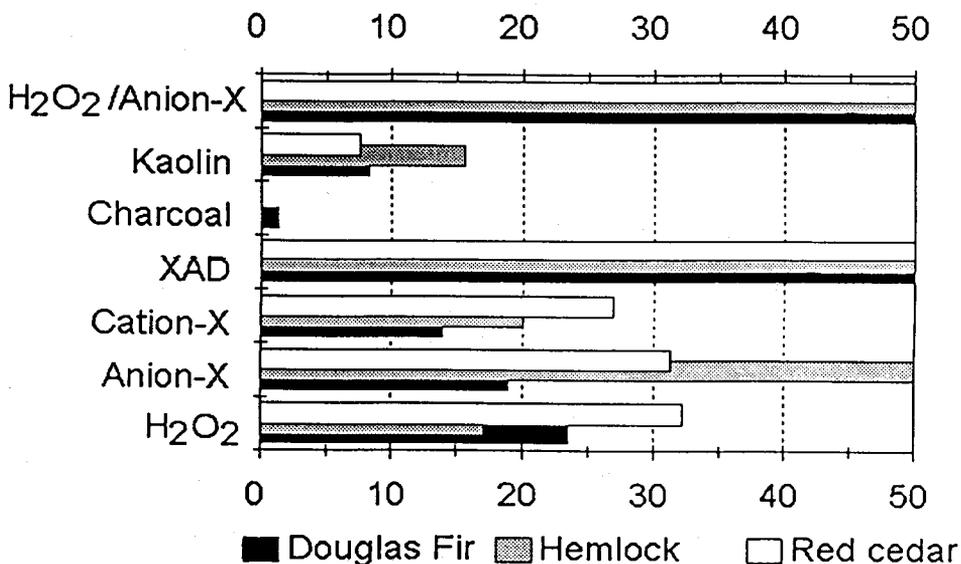


FIGURE 2. EC₅₀ removal.

Chemical oxidation reduced the COD of the three condensates by 40-60% (Figure 1). The greatest decrease was with the WRC condensate while the WH condensate was the least affected. Oxidation of the condensates also reduced the toxicity of all three wastewater (Figure 2). Accurate determinations of the EC₅₀ values required quenching of residual peroxide with sodium sulphite (Na₂SO₃). The EC₅₀ values of the quenched, oxidized condensates increased notably but were still between 16-30% suggesting that detoxification was incomplete. Again, residual COD and toxicity indicated that further treatment was required.

Chemical oxidation of organic material, such as some aromatics, by H₂O₂/Fe³⁺ can generate carboxylic acids (Vella and Munder 1993, Firth and Beckman 1990). Similar results were obtained with the RF/V condensates as indicated by the 1.5-2 fold increase in titratable acidity after H₂O₂ oxidation (Table 3). The use of subsequent anion exchange after oxidation should remove newly formed acidic moieties as well as the original acids that were present. Sequential H₂O₂ oxidation/anion exchange was done on all three condensates. Preliminary results showed that this sequence reduced the COD of all three condensates by over 95% (Figure 1). The sequential treatment strategy also detoxified all three condensates (Figure 2). Similar results were observed after scale up to 1 L (Table 4). Detailed comparisons between treated and untreated condensates confirmed the observation that sequential H₂O₂ oxidation/anion exchange effectively reduced both COD and BOD₅ by 70-90% (Fig.1 and 2, Table 4). This treatment also significantly reduced the Microtox toxicity of all three condensates.

TABLE 3. Titratable acidity (expressed as grams of NaOH required to neutralize 1 L of condensate) of three RF/V condensates before and after H₂O₂/Fe³⁺ oxidation.

Titratable Acidity (mg NaOH/L condensate)		
	Untreated	Oxidized
Douglas-fir	440	640
Western Red Cedar	150	380
Western Hemlock	150	340

The effect of oxidation/anion exchange on condensate toxicity towards *Daphnia magna* gave mixed results (Table 4). Although the WH condensate was completely detoxified by this treatment and the toxicity of the DF was noticeably reduced, the treated WRC condensate was as toxic as the untreated condensate. Further studies on the nature of the toxicants in WRC condensates may be required to optimize their removal. The sequential H₂O₂ oxidation/anion exchange treatment raised the pH of the three condensates to well over 11.5 (Table 4). However, the treated condensates had very low buffering capacities and were easily neutralized with HCl (< 3 mgL⁻¹).

TABLE 4. Characterization of three RF/V condensates before and after H₂O₂ oxidation/anion exchange.

	Douglas-fir		Western hemlock		Western redcedar	
	Before	After	Before	After	Before	After
COD in mgL ⁻¹ (+ /std)	1456 (33)	314 (20)	585 (36)	72 (7)	873 (88)	303 (20)
BOD ₅ in mgL ⁻¹ (+ /std)	651 (90)	< 60 (0)	173 (50)	< 60 (0)	231 (70)	< 60 (0)
pH	4.4	12.0	4.0	12.3	4.0	11.6
Microtox - EC ₅₀	2.4%	> 50%	10%	> 50%	6%	> 50%
<i>D. magna</i> - LC ₅₀	9%	43%	27%	100%	23%	26%

Conclusions

Condensates collected during the RF/V drying of three British Columbia wood species were evaluated for their compliance with B.C. wastewater discharge regulations. All three condensates were acidic (pH 4.9-5.6), had a biological oxygen demand (110-224 mg of O₂ per L⁻¹) and were acutely toxic towards *Daphnia magna* (LC₅₀ 9-25%) and *P. phosphoreum* (1.7-2.8%). The condensates therefore require some form of treatment prior to discharge, as defined by legislation in British Columbia and many parts of North America.

A series of physic-chemical treatments were evaluated for their ability improve condensate quality to a point where discharge would be permitted. Sequential H₂O₂ oxidation/anion exchange is considered to be the most effective physic-chemical treatment evaluated in this study. However, WRC condensates were still toxic towards *Daphnia magna* suggesting that further treatment may be required. At present, the laboratory scale treatments can only generate 500 ml of treated condensates before regeneration is required. Scale up studies are necessary for a proper assessment and optimization of sequential H₂O₂ oxidation/anion exchange treatments. In particular sufficient volumes (~20 L) of treated condensates must be generated for fish toxicity assays. This is essential as the Microtox assay serves only as an indicator of relative detoxification and cannot substitute for actual fish toxicity studies. Other treatment strategies also warrant further investigation, most notably the use of hydrophobic adsorbents such as the XAD resin. The identification of organic compounds in RF/V condensates was not investigated but deserves further study. The monitoring of such compounds may aid in the development of drying regimes as well as in assessing waste water treatment strategies.

References

American Public Health Association (APHA). 1985. Standard methods for the examination of water and wastewater (16 th ed.), Washington, D.C.

- Avramidis, S., and R. Zwick. 1992. Exploratory radio-frequency/vacuum drying of three B.C. coastal softwoods. *Forest Products J.* 42(7/8):17-24.
- Avramidis, S., F. Liu and B. Neilson. 1994. Radio-frequency/vacuum drying of softwoods: drying of thick western redcedar with constant electrode voltage. *Forest Products J.* 44(1):41-47.
- Carey, J. 1992. An introduction to advanced oxidation processes (AOP) for destruction of organics in wastewater. *Water Poll. Res. J.* 27(1):1-21.
- Carter, R. and J. Hyder. 1993. Treated kaolin combines effective pitch control with handling ease. *Pulp and Paper (Nov)*: 87-90.
- Chaplin, M.. 1986. Monosaccharides. *In*: Carbohydrate Analysis: A practical approach. ed: M. Chaplin and J. Kennedy. IRL Press. Oxford, pp. 1-36. Environment Canada. 1990. Biological test method: Acute lethality test using *Daphnia* spp. Reference method EPS /1/RM/11.
- Environment Canada. Environment Canada. 1992. Biological test method: toxicity test using luminescent bacteria (*Photobacterium phosphoreum*). Reference methods EPS 1/RM/24. Environment Canada.
- Fein, J., K. Omotani, H. Hunter, J. Buckholz and D. Potts. 1994. Toxicity identification and reduction for two fine paper mill effluents. *In*: Proceedings of TAPPI International Environmental Conference. Portland, OR. April 17-20. pp. 889-922.
- Firth, B. and C. Beckman. 1990. Comparison of Microtox testing with rainbow trout (acute) and *Ceriodaphnia* (chronic) bioassays in mill waste water's. *Tappi J.* 169-174.
- Koyama, O. Y. Kagamagat and K. Nakamura. 1994. Degradation of chlorinated aromatics by Fenton oxidation and methanogenic digester sludge. *Water Res.* 28(4):895-899.
- Liu, F., S. Avramidis and R. Zwick. 1994. Drying thick western hemlock in a laboratory radio-frequency/vacuum dryer with constant and variable electrode voltage. *Forest Products J.* 44(6):71-75.
- Singer, J., J. Jackson and R. Rice. 1995. Investigation of potential toxicity and mutagenicity of distillates from drying of five species of wood. *Forest Products J.* 45(5):45-50.
- Vella, P. and J. Murder. 1993. Uses of $KMnO_4$, H_2O_2 and ClO_2 in wastewater applications in the nineties. ed: Eckenfelder, A. Bowers and J. Roth. Nashville, Ten. Pub., Technomic Pub., Lancaster PA. pp 222-238.
- Voss, R. and A. Rapsomatotis. 1985. An improved solvent-extraction based procedure for the gas chromatographic analysis of resin and fatty acids in pulp mill effluents. *J. Chromatography* 346:205-214.

Walling, C. 1975. Fenton's reagent revisited. *Accounts of Chemical Research* 8:124-131.

Wang, E. and J. Chen. 1992. A study on the treatment of bleach effluent with Fenton reagent. In: *Proceedings of the 7th International Symposium on Wood and Pulping Chemistry*, Beijing, China. May 25-28. pp. 934-931.

Wastney, S. 1994. Emissions from wood and biomass drying: a literature review. International Energy Agency Task X.

Zwick, R. and S. Avramidis. 1993. Radio frequency/vacuum drying of thick lumber. In: *Proceedings of the globalization of wood: supply, processes, products, and markets*. Forest Products Society and Oregon Forest Resources Institute. Nov 1-3, Portland, Oregon. pp 80-86.