# BIODEGRADABILITY OF WASTEWATERS FROM A MEDIUM-DENSITY FIBREBOARD MILL

T.I.JAMES* and J.R.L.WALKER†

Department of Plant & Microbial Sciences, University of Canterbury,
Private Bag, Christchurch, New Zealand

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ABSTRACT

The effluent from a medium-density fibreboard mill, using *Pinus radiata* D.Don as the chief source of raw material, has been analysed for total and suspended solids, particle size distribution, reducing sugars, total carbohydrate, nitrogen, and phosphorus. The waste liquors, which contained many fine cellulose fibres, were moderately biodegradable with $BOD_5$/COD ratios from 0.49 to 0.22. Microbial utilisation of the raw wastewater was enhanced by supplements of nitrogen whereas addition of phosphate had little effect.

**Keywords**: biodegradation, wastewater treatment, board mill wastewater, thermo-mechanical pulping.

## INTRODUCTION

For some time the disposal of liquid wastes generated by the pulp and paper industry has been a matter of environmental concern and Cox (1981) has presented a report on the nature and environmental impacts of waste liquors from pulp and paper mills using *P.radiata* feedstocks. Matters of concern include possible toxicity (especially to fish), water clarity, and foaming. A limiting factor in any biological treatment of sludge from pulp mills is the availability of microbes capable of rapidly degrading the lignocellulose of the wood pulp fibres (Harkin *et al.* 1974).

This report is concerned with a biochemical/microbiological study of the mill wastewater from a medium-density fibreboard mill operated by Canterbury Timber Products Ltd (CTP), Rangiora. In this mill wood chips are converted to fibre by a thermomechanical pulping (TMP) process and the fibre is blended with synthetic resins to produce a wood-based panel (Customwood™). An abbreviated flow chart showing the major sources of wastewaters is given in Fig. 1.

The wastewater from the TMP process contains soluble compounds derived from the wood chips (mostly *P. radiata*) plus particulate "fines" derived from the chip washing and digestion unit. At present this raw wastewater is mixed with domestic sewage (6:1 v/v) and

* Current address: C/-Woodward-Clyde (NZ) Ltd, P.O. Box 37 547, Parnell, Auckland.

† To whom correspondence should be addressed

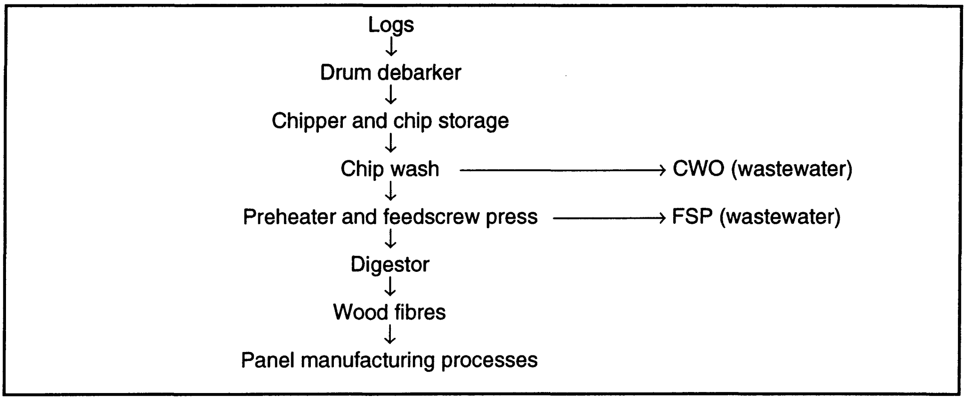


FIG. 1–Major sources of wastewaters in the medium-density fibreboard process

treated in an aeration basin equipped with floating aerators. It is then held in a storage pond until it is spray-irrigated on to grass pastures during the summer (November to March). From the onset (1984) of this disposal procedure no obviously adverse reactions have been observed in the wastewater-irrigated pastures.

Spray-irrigation of the Tasman Pulp and Paper Company Ltd's kraft pulp mill wastewater produced a large pasture growth response in summer, with improved pasture composition and significantly reduced effluent BOD* (Johnson & Ryder 1988). Shields *et al.* (1986) found that spraying primary-treated pulp mill effluent caused a 41% increase in forest tree height whilst a mix of treated and non-treated effluent caused a 68% increase, as compared to non-sprayed controls.

Previous analyses of the CTP mill wastewater and treatment systems (extended aeration basin and oxidation/storage pond) by R.Hoyle (unpubl. data) are summarised in Table 1.

## Possible Utilisation of Pulp Mill Waste Liquors

Expenditure on effluent treatment can be minimised by exploring the possibilities of waste utilisation (Forster 1975). For example, lignocellulosic wastes have potential for biological exploitation but this is limited by the slow microbial utilisation of cellulose and the high cost of pretreatment to improve degradability. Lignin has less potential for biotechnological use and its presence in wastes is often a problem (Knapp 1985). In practice, the bioconversion of lignocelluosic wastes may become economic only when there is a disposal cost to the producer (Ek & Eriksson 1980).

It is possible to use pulp mill wastes as feed binders, mostly in the pig and poultry industries. Nutritional and health implications have been discussed by van der Wal (1983) since some wood extractives may be toxic. Also, low-molecular-weight phenolics can affect digestibility and have been found to inhibit ethanolic fermentation by the yeast *Saccharomyces cerevisiae* (Clark & Mackie 1984).

* BOD = biological oxygen demand: amount of oxygen consumed by micro-organisms in the chemical oxidation of organic matter over a given time period.

TABLE 1–Analysis of CTP mill effluent treatment system

| | Raw liquor | Aeration basin | Storage pond |
|---|---|---|---|
| Flow rate ($m^3$/day) | 190 | 190–200* | 190–200 |
| Discharge temperature | 105°C | ambient | ambient |
| Residence time | n/a | 30–40 days | 6 months |
| Volume ($m^3$) | n/a | 10 000 | 30 000 |
| $BOD_5$ (mg/l) | 30 000 | 4 000 | 1 120 |
| COD (mg/l) | nd | 8 130 | 3 090 |
| Soluble solids (mg/l) | 1 000 | 5 100 | 670 |
| Settleable solids (mg/l) | nd | 3 100 | 880 |
| N organic†.(mg/l) | 53 | 47 | 57 |
| P total (mg/l) | 29 | 41 | 16 |
| pH | 4.5 | 6.6 | 5.8 |

Mineral nutrients in aeration basin wastewater (mg/l)—Ca 85.0, Cu 0.5, Fe 0.8, Mg 5.5, Mn 1.3, K 18.0, Na 44.0, Zn 0.5.

nd=not determined

* Continuous input into ponds until time of emptying. Storage pond filled continuously from April to October (winter); treated wastewater spray-irrigated from November to March (summer).

† Most nitrogen present in bound (organic) form, only traces as nitrate, nitrite, or ammonia.

Conversion of cellulosic wastes to glucose syrups is still being actively researched but the economics of using waste liquor for ethanol production are dependent on the cost of biomass, rate of enzymic conversion to glucose, enzyme production cost and recovery, and the potential to ferment xylose (Wilke *et al.* 1981; Lee & McCaskey 1983).

Yet another possibility is the use of industrial wastes with high BOD for the production of microbial biomass protein (MBP) for animal feedstuffs, but this is still new in New Zealand (Kennedy 1985). Overseas researchers (Crawford *et al.* 1973; Bellamy 1974) have found thermophilic actinomycetes which actively decomposed cellulose and grew well on pulping fines. Under fermentative conditions 60–65% degradation of fines occurred after 96 h, yielding a product containing 30% protein and in which 88% of the original suspended solids had been converted into MBP. In general, sulphite and kraft pulp mill waste liquors are better suited for the production of MBP because their carbohydrates include soluble sugars produced by the hydrolysis of cellulose and hemicelluloses during pulping. For example, the Pekilo Process (Romantschuk & Lehtomaki 1978) uses an anaerobic, fluidised-bed bioreactor with bacteria specifically adapted to the waste being treated.

## Biochemical Characteristics of CTP Mill Wastes

The wastewater from the digestion process at CTP is derived mostly from *P. radiata* wood; thus, it was expected to contain lignocellulose, hemicelluloses, and some low-molecular-weight soluble sugars, amino acids, etc.

Bjorklund Jansson (1980) and Bjorklund Jansson & Back (1975) found that the total solids in two white waters from a fibreboard mill processing mostly *Pinus silvestris* L., contained carbohydrate (50%), lignin-like material (15–20%), and inorganic constituents (2–5%). Bjorklund Jansson (1980) characterised the biochemical changes occurring during treatment with activated sludge and trickling filter systems and concluded that this waste was moderately biodegradable. Hydrolysis of coniferous wood yields mainly hexoses (glucose, mannose, and traces of galactose) in contrast to angiosperm hardwoods which yield almost equal amounts of hexoses and pentoses, mostly xylose with some arabinose (Sjostrom 1981). Harkin *et al.* (1974) found that aspen (*Populus tremula* L.) groundwood pulp waste liquor contained glucose (75%) and xylose (20%); groundwood pulping waste is similar to that from thermomechanical pulping.

The BOD of pulp mill waste liquor depends on process conditions but the liquor is usually reasonably biodegradable; however, there can be considerable oxygen depletion at the point of discharge. The BOD of paper mill waste liquors is due mostly to substances in solution since removal of suspended solids reduced the BOD by less than 20% (Callely *et al.* 1977). By contrast, suspended solids make a greater contribution in pulp mill waste liquors. Bark is known to create a high BOD.

Some objectives of the study reported here were:

(1) Characteristion of major biochemical and physical properties of CTP waste liquor;

(2) Possible use of waste liquor for animal feed or MBP production;

(3) Investigation of factors affecting the biodegradability of raw waste water.

## MATERIALS AND METHODS

Sampling: composite samples for analysis were taken from the preheater feedscrew press, chip wash overflow, aeration basin, storage pond.

Total solids: samples of raw mill waste liquor were freeze-dried for 48 hours, or oven-dried at 105°C, and then weighed.

Suspended solids: samples were clarified in a Sorvall RC2C refrigerated centrifuge at 16 000 g for 40 min and then the supernatant was freeze-dried and weighed.

### Particle Size Distribution

The Coulter counter (Model TA) measures the changes in resistance which occur when a suspension of particles in a saline solution is drawn through a fine glass orifice; the increase in resistance is proportional to the particle volume. Because the particle size variation was so large, particles had to be analysed in two size groups; this was achieved by pre-filtering the raw sample through a 200-μm membrane filter.

Microscopic analysis was carried out to complement the Coulter counter analysis. Using the whole sample, all particles in 20 microscope fields at ×10 and ×100 magnification were recorded.

### Chemical and Biochemical Methods

*Total carbohydrates*

These were estimated as equivalent glucose by the anthrone method (Colowick & Kaplan 1957a). Hexuronic acids reacted only slightly and amino-sugars do not react with this reagent.

*Pentose sugars*

Pentosans were hydrolysed by distillation with acid and the resulting furfural was determined by Mejbaum's orcinol method (Colowick & Kaplan 1957b).

*Reducing sugars*

In order to assess the potential of the waste liquor as an ingredient for animal feed, or as a substrate for growth of microbial biomass, it was necessary to compare the total sugars with the total reducing-sugars and glucose. Reducing-sugars were assayed by the PAHBAH method (Lever *et al.* 1973) in which reducing-sugars react with 4-hydroxybenzoic acid-hydrazide in alkali to form aroylosazones which yield yellow complexes with $Ca^{2+}$. Absorbance was measured at 420 nm.

*Glucose*

Glucose was assayed by the specific glucose oxidase method (Barton 1966).

*Nitrogen*

Nitrogen was measured by the Kjeldahl method (Colowick & Kaplan 1957c).

*Inorganic phosphate*

Inorganic phosphate was assayed via its reaction with ammonium molybdate in an acid solution to form phosphomolybdic acids. Addition of a reducing agent reduces the molybdate to give a blue colour. Absorbance was measured at 80 nm (Colowick & Kaplan 1957d).

## Oxygen Demand Experiments

Oxygen demand is caused by carbonaceous organic matter, oxidisable nitrogen compounds, and certain reducing compounds.

*Biological oxygen demand (BOD)*

The 5-day biological oxygen demand ($BOD_5$) was measured using the "Winkler" method (APHA 1975).

*Chemical oxygen demand (COD)*

This test measures the total oxygen consumed by the sample when fully oxidised by boiling with acidic dichromate solution (APHA 1975).

*Total organic carbon (TOC)*

The $CO_2$ released by the total oxidation of carbon compounds was measured using a non-dispersive infra-red analyser (APHA 1975).

## Qualitative Analyses

The soluble sugars present in the mill waste liquor were analysed by one- or two-dimensional chromatography on cellulose thin layers (TLC) (Dawson *et al.* 1986) developed in iso-propanol/water (1:4 v/v) or acetonitrile/water (1:4 v/v).

Sugars were revealed with the following chromogenic spray reagents:

(a) Aniline phthalate—to detect reducing sugars, aldopentoses, aldohexoses, deoxy-sugars, and uronic acids;

(b) Naphthoresorcinol—to detect ketoses and uronic acids.

## Respirometric Experiments

In an attempt to investigate the biodegradability of the waste liquor, the rate of $CO_2$ production was recorded when soil and/or wastewater samples (50 g, or equivalent dry wt) were incubated in the dark at 25°C, with or without supplementary mineral nutrients. This was accomplished by the respirometric/titrimetric method of McCallion & Walker (1987). Sterile perlite was mixed with liquid samples to provide a matrix for microbial growth, to avoid waterlogging and ensure aerobic culture conditions. Supplementary nitrogen and/or phosphorus was added to some experiments as ammonium sulphate or potassium dihydrogen phosphate. Each experiment was carried out in triplicate.

# RESULTS AND DISCUSSION

## Characterisation of Mill Waste Liquor

Microscopic examination revealed fibre particles from 0.2 µm to 4.5 mm whilst a distribution analysis by the Coulter Counter showed many small particles and fewer large fibres with the majority (approx. 60%) in the range 10–25 µm. The presence of such small fibre particles should be favourable to microbial degradation.

Analyses of mill waste liquors are summarised in Tables 2 and 3.

The results for total carbohydrates were comparable to those of Bjorklund Jansson (1980) who found that carbohydrates made up only 16% of the total solids in a fibreboard mill waste water. Chromatographic analyses of the feedscrew press liquor revealed the presence of

TABLE 2–Analyses of mill waste liquors (mg/l)

| | Chip wash overflow | Feedscrew press |
|---|---|---|
| Total solids: by freeze-drying | 18 600 | nd |
| by oven-drying | 17 545 | 17 575 |
| Suspended solids | 5 500 | 4 500 |
| pH | 5.5 | 5.4 |
| Total carbohydrates | 470–6600 | |
| Reducing sugars | 225–634 | |
| Glucose | 1.5 | |
| Pentoses | 7.9 | |
| Total nitrogen | 53.0 | |
| Total inorganic phosphorus | 29.0 | |

(nd=not determined)

TABLE 3–pH, $BOD_5$, COD, and TOC of mill wastewaters

| Sample | pH | $BOD_5$ (mg/l) | COD (mg/l) | TOC (mg/l) | $BOD_5$/COD |
|---|---|---|---|---|---|
| Chip wash overflow | 5.5 | 9800 | 20 226 | 49 800 | 0.49 |
| Feedscrew press | 5.4 | 8000 | 21 300 | 44 293 | 0.38 |
| Aeration basin | 6.5 | 3050 | 3 750 | 1 630 | 0.22 |

xylose and arabinose plus traces of glucose, fructose, rhamnose, sucrose, maltose, and glucuronic acid.

The pH difference between chip wash overflow and feedscrew press raw liquors (pH 5.4–5.5) and the aeration basin (pH 6.7) could be explained by the addition of raw sewage (from the mill) which neutralised the slightly acidic raw liquor, plus the buffering effects of aeration and microbial growth.

Most biological industry effluents show $BOD_5$/COD ratios in the range 0.2–0.5:1 (Callely *et al.* 1977) and the present results (Table 3) are within this range. This suggests that the feedscrew press liquor was moderately biodegradable whilst the observed decrease in $BOD_5$/COD ratios of the raw liquor to that of the aeration basin suggests that the system was performing adequately.

## Respirometric Experiments

In an attempt to assay the effect of mill waste liquor on microbial growth in different soils, the rates of $CO_2$-evolution were compared before and after addition of waste feedscrew press liquor (Fig.2). The initial increase in respiration rate could be due to the utilisation of the more readily metabolised sugars and other nutrients in the first 6 days, followed by a phase of nutrient-limited microbial growth. Similar experiments with the other waste liquors revealed little difference in repiration rates between the various samples.

Other experiments (Fig. 3) were carried out to investigate the effect of supplements of nitrogen (as $NH_4^+$), phosphate, and nitrogen plus phosphate, to raw feedscrew press liquor, since these are frequently the limiting nutrients in natural microbial ecosystems. Nitrogen availability appeared to be a limiting factor for the microbial degradation of the raw waste

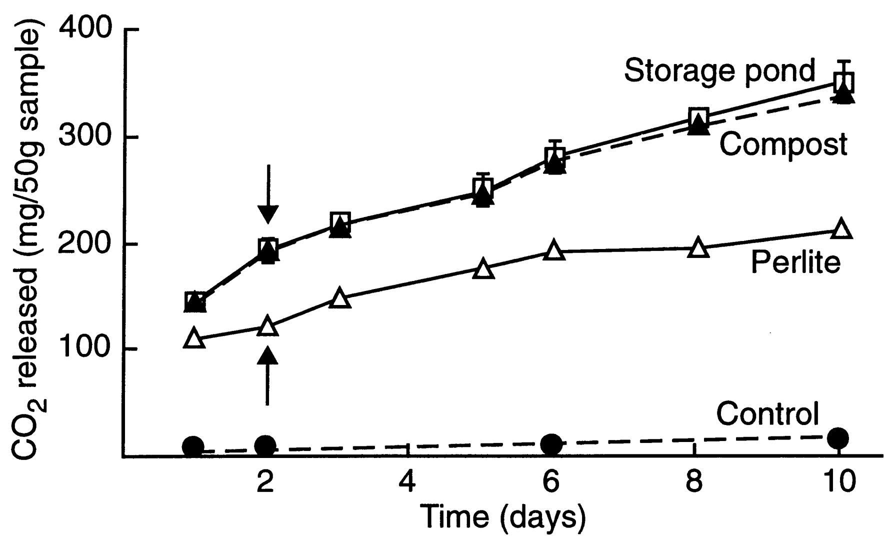


FIG. 2–Rates of $CO_2$ evolution from soil samples incubated with feedscrew press liquor (arrow indicates time of addition). Perlite plus water as control.

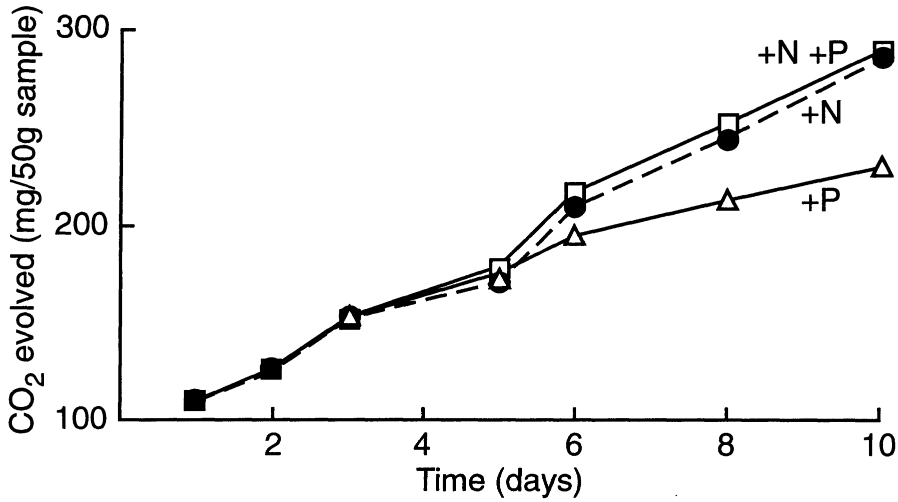


FIG. 3–Effect of added mineral nutrients on rates of $CO_2$ evolution from feedscrew press liquor. Nutrient additions were $(NH_4)_2SO_4$ (1.0 g/l) (+N), $KH_2PO_4$ (2.0 g/l) (+P), or both (+N+P). Perlite as the support matrix.

liquor samples but not for aeration basin samples. Further, since phosphorus levels were adequate, the results suggest that microbial growth was probably carbon limited which is how it should be for maximum BOD reduction.

## CONCLUSIONS

The results from this project suggest that the TMP mill waste liquor is too low in soluble sugars to be useful for the production of microbial biomass proteins (Kennedy 1985) or, after concentration, for use as an animal feed additive.

The ratio of soluble reducing-sugars to total carbohydrate seems to be an important parameter for determining the BOD and therefore the biodegradability of an effluent. Biodegradation is probably favoured by the continuous discharge of wastewater into the aeration basin leading to a more stable microbial environment.

The respiration experiments indicated that nitrogen was a limiting factor for the raw waste liquor but not the aeration basin samples (probably because of the addition of sewage). Adding exogenous nitrogen may have increased respiration because it was in a more-available form, even though nitrogen levels were of the right order of magnitude to facilitate biodegradation.

The operating conditions of the present TMP process limit the options for utilisation of the mill waste liquor but, contrary to earlier studies and predictions (K. Chapman, pers.comm.), visual indications suggest that the soils irrigated with waste liquor have not become more anaerobic, clogged, or less productive. Therefore, the existing effluent treatment system may be considered effective in terms of effluent biodegradability, nutrient balance, and microbial growth.

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