Assessment of air emissions from industrial kiln drying of *Pinus radiata* wood

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The nature and mass flows of atmospheric emissions from an industrial kiln, drying radiata pine (*Pinus radiata* D. Don) at 100 °C dry bulb and 70 °C wet bulb, were assessed by measuring the concentration of chemical components in the kiln atmosphere at regular time intervals and determining air-flows and temperature differentials across the stack. The volatile organic compounds (VOC) were trapped on activated carbon and analyzed by GC-MS. The aldehydes were trapped in 2,4-dinitrophenol-hydrazine solution and the aldehyde derivatives analysed by HPLC. Polar compounds were trapped in water and then alcohols were analysed by GC and organic acids by ion exchange chromatography. The two major VOC found were α-pinene and β-pinene, which made up 90% of the total discharge (405 g/m^3 wood). Most of the VOC fraction was released during the early stages of drying. The release of potentially hazardous components (formaldehyde, acetaldehyde, furfural) was found to be relatively low (1.1, 8.7, and 0.1 g/m^3 wood, respectively) provided the kiln emissions are well dispersed, these levels of release are unlikely to cause adverse environmental effects.

Abschätzen der Luftemissionen beim industriellen Trocknen von Kiefernholz

Art und Menge der gasförmigen Emissionen während des industriellen Trocknens von Kiefernholz (*P. radiata* D. Don) wurden abgeschätzt. Die Trockentemperatur betrug 100 °C, die Feuchttemperatur 70 °C. Chemische Komponenten in der Ofenluft wurden in regelmäßigen Zeitintervallen gemessen sowie die Luftbewegungen und Temperaturdifferenzen innerhalb des Holzstapels bestimmt. Die flüchtigen organischen Bestandteile (VOC) wurden an Aktivkohle adsorbiert und mittels GC-MS analysiert. Aldehyde wurden in Lösungen von 2,4-Dinitrohydrazin aufgefangen und die entsprechenden Aldehydderivate mittels HPLC analysiert. Polare Komponenten wurden in Wasser absorbiert, wonach die Alkohole mittels GC und die organischen Säuren mit Ionenaustauschern aufgetrennt wurden. Die Hauptkomponenten der VOC waren Alpha- und Beta-Pinen, die zusammen 90% des Massenverlustes (405 g/m^3 Holz) ausmachten. Die Hauptmenge wurde im frühen Trockungsstadium freigesetzt. Die Freisetzung von eventuell schädlichen Komponenten war relativ gering (Formaldehyd 1,1 g/m^3, Acetaldehyd 8,7 g/m^3 und Furfural 0,1 g/m^3). Wenn die Ofenabluft gut verdünnt ist, sollten diese Mengen kaum Umweltschäden verursachen.

1
Introduction

Demand for dried lumber has increased markedly in New Zealand over the last 5 years due to export requirements and increased local demand for dry framing. Controlled drying of lumber is important to minimise shrinkage and distortion of products, minimise degradation of timber, to precondition timber prior to copper-chrome-arsenic preservation, to reduce transport costs for lumber and to improve re-manufacturing and finishing qualities.

Increasingly, operators of kilns are being required to obtain permits for air emissions, to comply with more stringent controls or environmental monitoring conditions. In New Zealand, the Resource Management Act (1991), stipulates that actions for "avoiding, remedying or mitigating any adverse effects of activities on the environment" must be undertaken. Therefore, assessment of potential environmental effects arising from kiln-drying lumber is important for resource permits.

Environmental effects may arise from timber drying due to discharges of: hazardous compounds (e.g. formaldehyde); volatile organic compounds (VOC); compounds contributing to blue haze; odorous substances; aqueous condensates; and inorganic contaminants. Recently a series of studies in the USA has been undertaken to determine the extent of carbon discharge from kiln drying of lumber using the Environmental Protection Agency (EPA) method 25A (NCASI 1996; Shmulsky 2000a, b, c; Ingram et al. 2000). This method is specific for hydrocarbons and assesses the kiln's atmosphere using flame ionisation to estimate the extent of emissions as carbon. However, Word et al. (1998) has highlighted some issues about the appropriateness of the method. The presence of compounds such as formaldehyde, formic acid, and methanol give a poor detector response and can lead to underestimating the levels of emissions.

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Apart from steam, hydrocarbons are the predominant group of compounds released during timber drying. Emissions from driers are complex, containing gaseous and aerosol organic compounds. Monoterpenes are the principal volatile organic compounds (VOCs) released, of which β-pinene is typically the major component (Cronn et al. 1983; McDonald and Wastney 1995; McDonald et al. 1999a). Despite low vapour pressures, significant quantities of non-volatile compounds, such as long chain fatty acids, are also found in emissions (Banerjee et al. 1995; McDonald and Wastney 1995), as these are driven off via steam distillation.

Organic emissions arising from wood drying may result from the flash-off of natural volatile components, by products of thermal degradation, or form due to degradation or transformation reactions with either in the kiln or ambient atmosphere. The boiling point of monoterpenes range from 150 to 180 °C and for resin and fatty acids typically greater than 300 °C (Perry and Green 1984). Although mono- and diterpenes have boiling points greater than operating temperatures of kilns, their presence in emission streams is attributed to their high vapour pressures. Though, it has also been observed that these compounds have an affinity to wood, which in turn reduces their concentrations in emission streams compared to that which may be predicted based on vapour pressure alone (NCASI 1983).

The second source of organic emissions is products of thermal degradation of wood. Based on chemical analyses of wood following thermal treatment, the various components (cellulose, hemicellulose and lignin) are stable and not susceptible to degradation at temperatures below 100 °C, but above this temperature all components have been shown to degrade. Formaldehyde forms from the thermal decomposition of lignin and carbohydrate material, and its formation is largely temperature dependent (Marutzky and Roffael 1977). The presence of acetic acid in wood derived emissions arises from O-deacetylation of wood hemicelluloses.

Studies concerning the fate of VOC in the atmosphere have shown atmospheric chemistry is complex and that degradation and transformation reactions may occur in the both gaseous and aqueous phases (Grosjean et al. 1992; Faust 1994). Harley and Cass (1994) indicated that some toxic compounds found in ambient air were formed in the atmosphere as oxidation products of other volatile organic compounds. For example, terpenes have been found to react rapidly with ozone or hydroxyl or nitrate radicals to yield different organic compounds. Oxidation products of α-pinene were found to be formaldehyde, acetone, pinonaldehyde and glyoxal (Grosjean et al. 1992).

Environmental concerns relating to discharges of volatile organic compounds arise since they are potential precursors for photochemical formation of ozone, other atmospheric oxidants and aerosols. Furthermore, some individual VOC are known or suspected to have adverse effects on human health (Harley and Cass 1994). The mechanism by which ozone is produced from hydrocarbons is unclear but it involves complex photochemical reactions between reactive hydrocarbons, nitrogen dioxide and sunlight (Lippmann 1991). However, it is uncertain to what extent hydrocarbons contribute to ozone formation since some terpenes have been shown to react with ozone to produce oxidised products and aerosols. This latter process may contribute to blue haze formation. Although compounds produced during drying of lumber are known to be toxic, for example formaldehyde, studies based on mutagenic and cytotoxic tests of kiln condensates have concluded that these effects are likely to be minimal (Rice 1995).

This paper presents the results of an investigation in which the chemical composition and extent of emissions liberated throughout the whole drying run from an industrial kiln drying radiata pine lumber were assessed. The kiln temperature schedule was 100 °C/70 °C.

2
Experimental

2.1
Kiln charge, drying conditions, and mass flow determinations

A 40.9 m^3 charge of rough-sawn (41 mm thick) random width radiata pine lumber was provided and dried in a commercial kiln. The kiln was a front-loading system using converted heat from low-pressure steam. Air was circulated through the kiln using a series of side-mounted fans (Fig. 1). A 100 °C dry bulb/70 °C wet bulb temperature schedule was employed with a 4.5 h presteaming/heating period at during which the vents were closed. The drying run was for 33 h. A random selection of 12 boards of lumber was sampled to provide information on initial and final moisture content, chemical composition of the wood and wood basic density. From the test pieces, at least 100 mm was removed and discarded from the ends of each sample, and cool stored in bags until analysis.

Although this approach overcomes some of the inherent difficulties of sampling kiln vents there are a number of key assumptions. These are:

(i) the atmosphere within the kiln chamber was completely mixed,
(ii) the composition of emissions at the exit point at any instant was the same as that in the kiln atmosphere (on the outlet vent side of the stack),
(iii) the drying rate within the kiln stack was uniform, and
(iv) the air velocity was independent of temperature.

The characteristics of the emissions were assessed by sampling the kiln atmosphere at specific time intervals and analysing for the constituents. Mass flow determinations were based on calculated values for the discharge flow rates of air. These were determined on eight representative fillet space dimensions, air velocity, and inlet and outlet temperatures through the timber stack were measured. The air humidity was determined by recording the temperatures of the air inlet and outlet, ambient air, and wet and dry bulb temperatures using thermocouples linked to a multi channel data logger (Fluke), which recorded at ten-minute intervals. The drying rate was obtained from this data by calculating airflow volume through the stack from dimensions of the spaces and air velocity. Velocity was measured prior to start-up using a calibrated hot wire anemometer (Kurtz model 441M). The weighted average air velocity was 3.85 m/s. All fillet spaces were classed as representing the edge or central spaces and the results
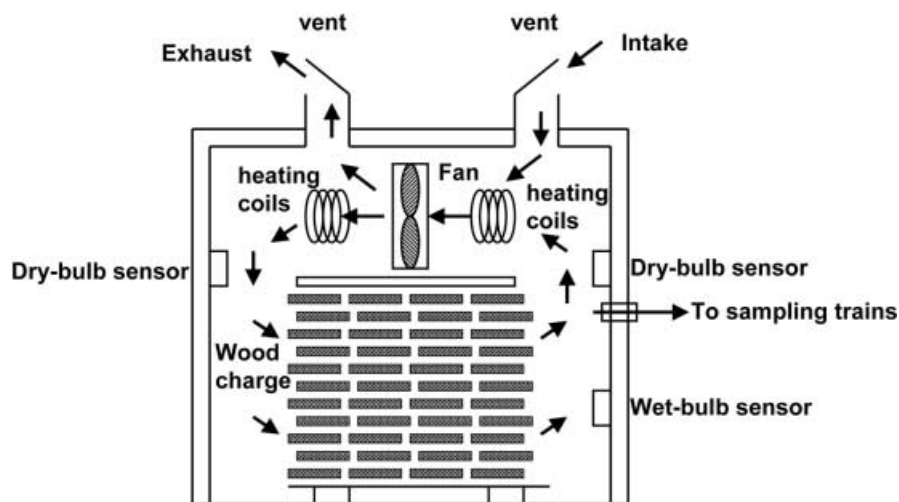
Fig. 1. Schematic diagram of the end view of the commercial kiln used showing the direction of airflow within the kiln and location of the sampling port
Bild 1. Schema des beladenen kommerziellen Trockners mit Luftbewegung und Probenentnahme

weighted accordingly. For each data point energy and mass balance calculations were performed to determine emission rates of air and moisture from the drier during the trial. The total amount of calculated moisture removed was summed and compared to the removal calculated from the stack initial and final moisture contents found from the collected samples of wood. The mass flow of organic components of the kiln atmosphere was then calculated from knowledge of its composition on a mass/volume basis.

2.2
Kiln atmosphere sub-sampling
The kiln atmosphere was sampled five times throughout the drying schedule by pumping a measured quantity of kiln vapour through appropriate impinger trains. Two holes were cut in the kiln wall 1.1 m above the floor near the centre of the kiln chamber (Fig. 1.). Three parallel sampling trains were used to sample for different chemical components as follows: (i) aldehydes were collected in acidified 2,4 dinitrophenylhydrazine (DNPH) (EPA method 0011 1990), (ii) polar compounds (methanol, ethanol, acetic acid and formic acid) were collected in chilled water impingers, and (iii) volatile organic compounds were collected by passing a sample stream successively through an empty impinger followed by an activated charcoal column (SKC, charcoal, coconut, 8 mm × 110 mm). The sampled atmosphere for each train was drawn through the collection trapping system, then through a desiccant tube followed by the pump and gas volume meter. The total volume of dry air and at ambient temperature drawn through each sample train was recorded. The mass unit volume of air of each component emitted was then calculated directly from the analytical results for the respective samples. All results are expressed on a dry air basis at 0 °C.

2.3
Chemical analyses
Aqueous solutions from the two chilled water impingers were combined and analysed for (i) acetic acid and formic acid by high performance anion exchange chromatography system (Dionex using a AS10 column) coupled to a conductivity detector and (ii) methanol and ethanol by

direct injection GC (Hewlett Packard 5890) onto a wide-bore capillary column (HP-1, 5 m), operating isothermally at 150 °C.

The DNPH solutions from the two impingers were combined and the derivatised aldehydes were then extracted into dichloromethane (25 mL, × 4). The dichloromethane extracts were combined, dried with anhydrous sodium sulphate, concentrated to a syrup, solvent exchanged with 1 portion of acetonitrile (5 mL), and re-concentrated to a syrup (EPA method 0011 1990; NCASI 1994). The mixture was made up to 25 mL with acetonitrile and filtered (0.45 μm) into a vial. Separation was performed on a C-18 column (Econosphere, Alltech, 150 mm × 4.6 mm, 5μ) connected to a Gilson HPLC system. Samples were eluted using a gradient programme starting with acetonitrile/water (60/40) for 10 min then increasing linearly over 5 min to 100% acetonitrile. The flow rate was constant at 1 mL/min. The DNPH derivatives were detected using UV absorbance at 360 nm. Formaldehyde and acetaldehyde were quantified by using calibration curves derived from a series of standard solutions.

Extraction and GC-MS analysis of volatile organics
The semi-volatile condensate sample (10–30 mL) was extracted with dichloromethane (5 mL, containing 100 μg/mL of DL-isoborneol as internal standard). The organic layer was removed and dried with anhydrous sodium sulphate for subsequent GC-MS analysis. The activated carbon trap (for VOC) was in two sections, each section was extracted with five 1 mL portions of dichloromethane (containing internal standard) and the extract from each section combined and analysed by GC-MS on a Hewlett Packard 5970 GC-MSD instrument. The volatile components were separated on an Ultra 2 (50 m × 0.25 mm) capillary column with a temperature programme of 40 °C (2 min) to 250 °C (30 min) at 4 °C/min followed by a second ramp to 300 °C (10 min) at 6 °C/min.

2.4
Micro steam distillation/extraction of wood sample
A composite wood sample (20 g wet weight) was steam distilled and the volatile compounds extracted into the

dichloromethane for 2 h by the method of McDonald et al. (1999a). The dichloromethane extract was analysed by GC-MS, as described above.

3
Results and discussion

3.1
Drying conditions
The wet lumber was pre-steamed for 4.6 h (with vents closed) after which the drying cycle was started and the vents were opened and then sampling commenced. Initial and final moisture contents of timber were 140% and 3.5% (dry basis) respectively. The calculated water loss based on the change in moisture content of the 40.9 m^3 of timber before and after drying was 24000 kg.

3.2
Air flow rates and drying rates
The rate of air entering and leaving the kiln was a function of kiln inlet and outlet air humidity and the drying rate of the wood stack. The air humidity was determined by measuring the wet and dry bulb temperatures of the ambient air, stack inlet and stack outlet. The drying rate was obtained from this data by calculating the air volume through the stack from dimensions of the fillet spaces and air velocity (Kininmonth et al. 1980; Shottafer and Shuler 1974). For each data point energy and mass balance calculations were performed to determine rates of air and moisture from the drier during the trial. The total amount of calculated moisture removed was summed and compared to the removal calculated from the stack initial and final moisture contents found from the collected samples of wood. The mass flow of organic components of the kiln atmosphere was then calculated from knowledge of its composition on a mass/volume basis.

Figure 2 shows the calculated volume of dry air (at 0 °C) being discharged from the kiln during the drying run. A summary of the airflow volumes discharged from the kiln during the run is given in Table 1.

3.3
Concentration of analytes and emission rates
To determine the concentration and emission rate of various components, it was necessary to combine data from air volume expelled from the kiln, air volume collected over kiln atmosphere sampling periods and the concentration of analytes in the various trapping systems.
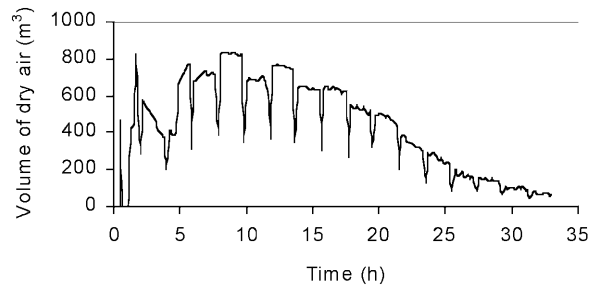

Fig. 2. Calculated volume of dry air (at 0 °C) discharged from kiln drying radiata pine at 100/70 °C in a commercial kiln
Bild 2. Berechnetes Volumen an trockener Abluft (0 °C) eines kommerziellen Trockners (*P. radiata*, 100/70 °C)

3.3.1
Aldehydes
The concentrations of the various aldehydes in the sampled kiln atmosphere are given in Table 2. Acetaldehyde was emitted at the highest concentrations at the start (16 mg/m^3 air) and end (20.5 mg/m^3 air) of the drying run. Air concentrations of formaldehyde ranged from 0.4 to 3.1 mg/m^3 air during the run and peaked both at the start and end of the run. Other aldehydes were at relatively low concentrations. Acetone (a ketone) and acrolein as DNPH derivatives co-eluted and their combined concentration given. Formaldehyde production results from thermal decomposition of lignin and carbohydrate material and is temperature dependent (Marutzky and Roffael 1977). The total amount of formaldehyde, acetaldehyde, and total aldehydes released during drying per volume of wood were 1.05, 8.66, and 17.9 g/m^3 of wood, respectively. Higher levels of aldehydes (20–31 g/m^3 green wood) were released during high-temperature (120 and 140 °C) kiln drying of radiata pine (McDonald and Wastney 1995). The emission rates (g/m^3 wood/h) of formaldehyde, acetaldehyde, and total aldehydes were relatively high following the pre-steaming stage (between 4.7 and 7.5 h) then dramatically fell by the second sampling period and continued to decrease with time (Fig. 3).

Formaldehyde is of most environmental significance as it is listed as a suspected carcinogen and now appears on the list of toxic air pollutants and has been shown to have chronic effects to humans at levels less than 0.4 mg/m^3 (MFE 1994).

The concentrations of formaldehyde at the vent outlets for much of the run was similar to or markedly lower than the New Zealand work exposure standard-time weighted average (WES-TWA) of 1.2 mg/m^3. The maximum concentration of acetaldehyde found during this study was 20.5 mg/m^3 air. This concentration is substantially below

Table 1. Calculated volumes of dry air (at 0 °C) released from a commercial kiln drying radiata pine at 100/70 °C
Tabelle 1. Berechnete Volumina an trockener Luft (0 °C), die von einem kommerziellen Trockner freigesetzt werden (*P. radiata*, 100/70 °C)

	Sampling periods					
	I	II	III	IV	V	Total
Mean sampling point (h)	5.7	9.2	14.0	25.2	29.7	
Air volume discharged from kiln during sampling (m^3)	1577	1746	1364	467	195	
Integration period (h)	4.7–7.5	7.5–11.7	11.7–19.7	19.7–27.5	27.5–33.0	
Integrated air volume discharged from kiln (m^3)	8286	12661	20397	9462	2234	53040

Table 2. Dry air concentration (at 0 °C basis) of methanol, ethanol, acetic acid, formic acid, formaldehyde and other aldehydes emitted from drying radiata pine in a commercial kiln at 100/70 °C

Tabelle 2. Konzentrationen in der trockenen Abluft (0 °C) an Methanol, Ethanol, Essigsäure, Ameisensäure, Formaldehyd und anderen Aldehyden. Emission eines kommerziellen Trockners bei 100/70 °C

Compound	Sampling period					
	I mg/m³air	II mg/m³air	III mg/m³air	IV mg/m³air	V mg/m³air	Total g/m³wood
Methanol	51.3	12.9	13.5	24.2	34.2	28.6
Ethanol	153	51.8	42.3	25.8	15.8	74.9
Formic acid	1.0		4.9	17.5	18.8	7.70
Acetic acid			6.9	31.5	43.5	13.1
Formaldehyde	1.26	0.36	0.41	1.31	3.14	1.05
Acetaldehyde	16.0	2.86	2.39	9.60	20.5	8.66
Acrolein + acetone	6.17	3.56	2.12	4.22	9.38	4.90
Propanal	2.15		0.52	0.93	0.36	0.93
Crotonaldehyde	0.25	0.055	0.092	0.44	0.83	0.26
Butanal	0.36	0.073	0.092	0.38	0.65	0.26
Benzaldehyde	0.48			0.17	0.32	0.15
Valeraldehyde	0.71	0.20	0.21	0.98	3.52	0.73
Hexanal	0.75	0.13	0.15	1.43	6.66	0.96

the WES-TWA of 180 mg/m³ (OSH 1994). Following the discharge of aldehydes from kiln vents substantial dilution with ambient air will occur.

3.3.2
Polar compounds

The concentrations of methanol, ethanol, formic acid, and acetic acid in the sampled kiln atmosphere are given in Table 2.

The total amounts of methanol and ethanol released over the whole run were 28.6 and 74.9 g/m³ of wood respectively. Methanol formation is the result of de-O-methylation of 4-O-methyl-D-glucuronic acid (Kosik et al. 1968) which constitutes about 1.6% by weight of radiata pine sapwood (Smelstorius 1974). The origin of ethanol is still unclear. Figure 4 shows that the majority of methanol and ethanol were released during initial stages of drying and reduced with time.

Although methanol is regarded as a human toxicant, its occurrence in kiln emissions is unlikely to cause adverse occupational or environmental effects. The maximum concentration of methanol emitted from the industrial kiln was approximately 51 mg/m³ air. This concentration is markedly lower than WES-TWA at 262 mg/m³ (OSH 1994).

The total amounts of acetic acid and formic acid released over the drying run were 13.1 and 7.7 g/m³ of wood,

respectively. The rate of acetic and formic acid released was shown to gradually increase with time (Fig. 5) and decrease at the final stage of drying.

The presence of acetic acid in the volatile kiln emissions arises from O-deacetylation of wood hemicelluloses (Lindberg and Rosell 1974). The value for acetic acid was slightly lower than that observed from kiln dried radiata pine at 120 and 140 °C schedules (22 and 38 g/m³ air) (McDonald and Wastney 1995). The maximum concentrations of formic and acetic acids occurred over the final sampling period (18.8 and 43.5 mg/m³ air respectively). These concentrations are slightly higher than WES-TWA of 9.4 mg/m³ and 25 mg/m³ for formic and acetic acids, respectively. Although these work place standards were exceeded, this only occurred at the later stages of drying when there was reduced venting.

3.3.3
VOC in wood

A composite wood sample from green and kiln dried timber were each analysed for monoterpenes. Total ion GC-MS chromatograms of VOC from green and kiln dried wood are shown in Fig. 6. These chromatograms indicate that the total amount of VOC in the dried wood is lower, and that the nature of compounds present is different. The total VOC concentrations in the green and dried wood
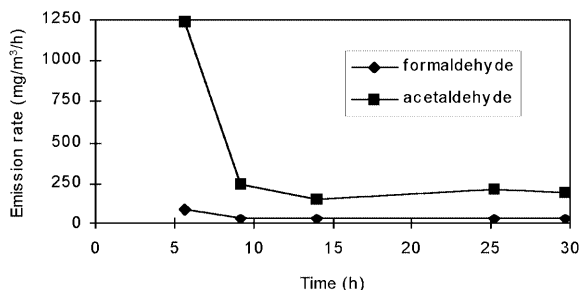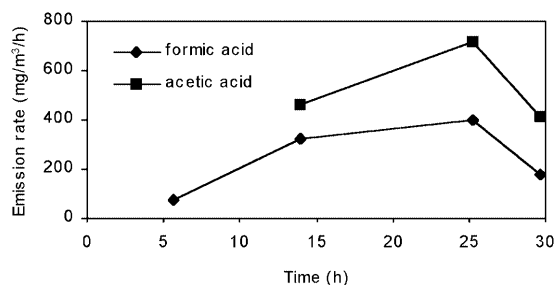
Fig. 3. Rate of formaldehyde, acetaldehyde, and total aldehydes released (mg/m³ wood/h) during kiln drying of radiata pine at 100/70 °C in a commercial kiln
Bild 3. Anteil an freigesetztem Formaldehyd, Acetaldehyd und Gesamt-Aldehyden (mg/m³ Holz) während des Trocknens von *P. radiata* in einem kommerziellen Trockner
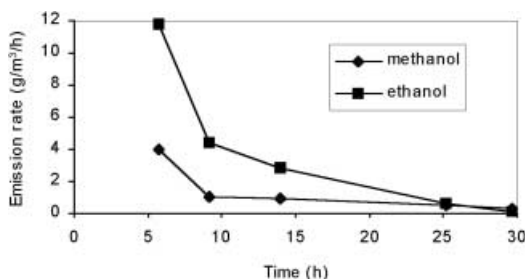
Fig. 4. Rate of methanol and ethanol released (g/m³ wood/h) during kiln drying of radiata pine at 100/70 °C in a commercial kiln
Bild 4. Anteil an freigesetztem Methanol und Ethanol (mg/m3 Holz) während des Trocknens von *P. radiata* in einem kommerziellen Trockner

Fig. 5. Rate of formic acid and acetic acid released (mg/m³ wood/h) during kiln drying of radiata pine at 100/70 °C in a commercial kiln
Bild 5. Anteil an freigesetzter Ameisensäure und Essigsäure (mg/m³ Holz) während des Trocknens von *P. radiata* in einem kommerziellen Trockner

were 239 g/m³ and 71.3 g/m³ wood respectively (Table 3). The main compounds identified in the green timber were α-pinene, β-pinene, limonene, β-phellandrene, 1,4-terpineol, and α-terpineol. In addition, to the monoterpenes, neutral diterpenes, such as pimarinal and methyl dehydroabietate were detected in the steam distillates. Higher levels of monoterepenes were found in the green lumber than previously reported for radiata pine, which ranged between 67 and 210 g/m³ wood (McDonald et al. 1999a). The main VOC in dried timber, in addition to those found in the green material were furfural and neutral diterpenes. Furfural is derived from degradation of pentoses, and its formation in wood is dependent on both pH and temperature.

3.3.4
Volatile organic compounds released during drying

The semi-volatiles and VOC collected in the charcoal traps were extracted into dichloromethane and analysed by GC-MS. The identity and concentrations of the VOC in the sampled kiln atmosphere are given in Table 3. Total ion GC-MS chromatograms of VOC extracted from the condensate and charcoal traps for sampling period II are shown in Fig. 7.

The main component identified in the condensate was α-terpineol (Fig. 7a). Other components found in this fraction were 1,4-terpineol, endo-borneol and fenchol. Most of the VOC were trapped on the charcoal cartridges. The major VOC found on the charcoal traps were α- and β-pinene (Fig. 7b). The presence of α-pinene, camphene, β-pinene and limonene were expected (Table 3) since these monoterpenes are common constituents of radiata pine (Burdon et al. 1992; McDonald et al. 1999a).

The air concentration of the two major compounds emitted, α-pinene and β-pinene, ranged from 53.7 to 228 mg/m³ and 120 to 474 mg/m³, respectively (Table 3). Concentrations of these compounds reduced about 3 fold between 6 and 9 h after the start of drying. The total amount of α-pinene, β-pinene and total VOC released during kiln drying were 119, 251, and 405 g/m³ of wood, respectively. However, this total is markedly higher than for values previously reported for drying radiata pine (120/70 and 140/90 °C) at approximately 35 and 66 g/m³ wood, respectively (McDonald and Wastney 1995). Lower values of total monoterpenes were also found during a study of condensate from a vacuum kiln, drying radiata

(a)

(b)
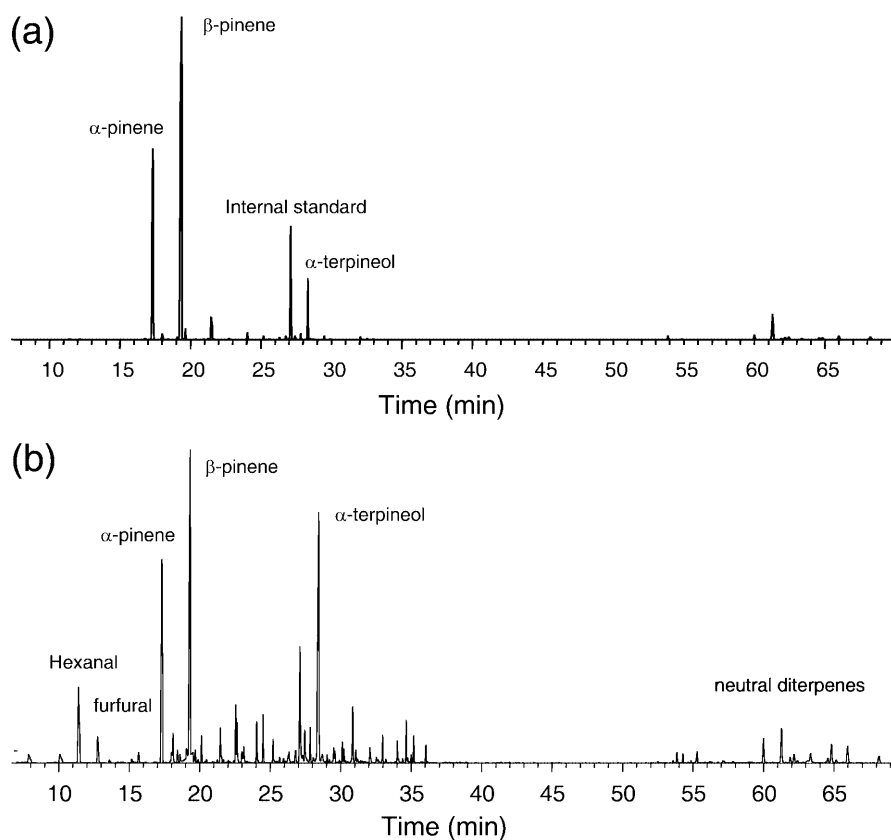
Fig. 6a, b. Total ion GC-MS chromatograms characterising (a) VOC from green radiata pine and (b) VOC from kiln dried radiata pine
Bild 6a, b. GC-MS-Chromatogramme der flüchtigen organischen Bestandteile (VOC) von von *P. radiata*; (a) waldfrisch; (b) nach dem Trocknen

Table 3. Dry air concentration (at 0 °C basis) of VOC from subsampled air samples and VOC levels in green timber and kiln dried timber from drying radiata pine in a commercial kiln

Tabelle 3. Konzentration an flüchtigen organischen Stoffen (VOC) in verschiedenen Abluftproben beim Trocknen von *P. radiata* in einem kommerziellen Trockner sowie Konzentrationen in waldfrischem und getrocknetem Holz

Compound	Retention time (min)	Sample I mg/m³air	Sample II mg/m³air	Sample III mg/m³air	Sample IV mg/m³air	Sample V mg/m³air	Total VOC g/m³wood	Green timber g/m³wood	Dried timber g/m³wood
Pentanal	7.89					0.37	0.02		0.52
1-Pentanol	10.21								0.53
Hexanal	11.42				0.48	2.35	0.24	0.14	3.28
Furfural	12.79					1.02	0.06		0.91
Hexenal	13.76								0.11
2-Heptanone	15.36								0.11
Heptanal	15.83								0.29
Tricyclene	16.83	2.05	0.28	0.15	0.13	0.78	0.65	0.20	0.05
α-Pinene	17.53	227.80	87.74	53.73	61.07	84.02	118.82	58.86	8.72
α-Fenchene	17.55					0.19	0.01		
Camphene	18.08	9.56	3.19	2.37	3.56	7.65	5.35	1.25	0.35
Heptenal	18.27								0.75
Benzaldehyde	18.61							0.11	0.30
Heptanol	18.75								0.25
Unknown	18.89								0.22
1-Octen-3-ol	19.22								0.80
Sabinene	19.31							0.64	
β-Pinene	19.71	473.85	188.20	120.06	120.43	165.09	251.01	145.72	13.48
Hepanoic acid	19.74								0.39
Myrcene + 2-pentyl-furan	19.69		2.61	1.41	1.58	3.16	2.05	1.57	0.40
Octanal	20.15					0.22	0.01		0.55
L-Phellandrene	20.45	0.53			0.12	0.24	0.15	0.06	0.04
Δ-3-carene	20.73	0.26				0.06	0.06	0.00	0.07
α-terpinene	20.97	0.71	0.22	0.15	0.31	0.75	0.40	0.08	0.03
Methyl (1-methylethyl)-benzene	21.31	1.44	0.41	0.32	0.55	1.15	0.77	0.10	0.07
β-phellandrene	21.65	29.16	7.34	5.05	5.68	9.61	12.54	5.00	0.88
2-Octenal	22.55					0.38	0.02		
Limonene	21.67							0.07	
Unknown (M, 126)	21.88								0.10
Unknown, 83,70,55,91,120	22.04								0.06
5-ethyldihydro-2(3H)-Furanone	22.65								0.05
2-Octenal (E)	22.73								1.31
γ-Terpinene	22.77	0.74	0.15	0.12	0.23	0.50	0.34	0.13	
Octanol	23.14								0.30
Nonanone	23.96								0.02
α-Terpinolene	24.08	2.96	0.62	0.60	0.89	1.80	1.40	0.92	
Monoterpene keteone (M, 152)	24.05								0.90
Fenchone	24.17	0.27					0.05		0.06
Nonanal	24.50					0.47	0.03		1.02
Unknown (M, 134)	25.07	0.18					0.04		
Fenchol	25.22	1.72	0.19	0.17	0.58	1.03	0.68	0.46	0.64
Allocimene	25.60	0.29				0.09	0.06		
Pinocarveol	26.36	2.27	0.21	0.15	0.25	0.47	0.69		0.19
Cis-sabinol	26.35	0.26					0.05	0.31	0.33
Camphor	26.63	0.40		0.05	0.07	0.09	0.12	0.05	
Monoterpene alcohol (M, 154)	26.80	0.74	0.08	0.13	0.19	0.27	0.30	0.44	0.43
Unknown (M, 150)	27.34	0.67	0.09		0.07	0.12	0.19	0.07	0.24
Endo-borneol	27.45	1.55	0.14	0.11	0.42	0.69	0.55	0.52	1.12
1,4-Terpineol	27.86	3.19	0.26	0.21	0.44	0.65	0.97	0.71	0.82
Unknown (M, 150)	28.04	0.20				0.08	0.04	0.05	0.20
Unknown, (M, 137)	28.21	0.17					0.03		
α-Terpineol	28.36	19.61	2.05	1.82	3.96	5.33	6.72	9.97	13.06
Bornyl formate	28.53	0.08	0.16	0.24	0.11	0.13	0.22	0.07	
Myrtenol	28.62	0.75				0.24	0.16		0.50

Table 3. Continued

Compound	Retention time (min)	Sample I mg/m³air	Sample II mg/m³air	Sample III mg/m³air	Sample IV mg/m³air	Sample V mg/m³air	Total VOC g/m³wood	Green timber g/m³wood	Dried timber g/m³wood
6,6-Dimethyl-bicyclo-[3.1.1]hept-2-ene-2-carboxaldehyde	28.71	0.55			0.07		0.13		0.00
2,4-Nonadienal	29.24								0.18
Fenchyl acetate	29.52	0.58			0.07	0.18	0.14		
4,6,6-Trimethyl-bicyclo-[3.1.1]hept-3-en-2-one	29.21	0.10					0.02		0.09
Carveol	29.59								0.04
Fenchyl acetate	29.71							0.33	0.31
Ethyl-4-(1-methylethyl)-benzaldehyde	29.60	0.28				0.12	0.06		0.30
2-Decenal	30.86					0.13	0.01		
5-Pentyl-2(5H)-furanone	31.29								0.32
Endobornyl acetate	32.09	0.36				0.10	0.08	0.28	0.48
Decadienal	33.17								0.61
Monoterpene alcohol (M, 154)	34.23								0.49
Undecanal	34.66					0.05	0.00		0.89
Monoterpene ketone (M, 152)	35.37								0.61
Dimethoxy-propenyl-benzene	36.07	0.09					0.02		0.41
Vanillin	36.36								0.03
Sandaracopimaradiene	53.87								0.06
Pinosylvin dimethyl ether	54.13							0.58	0.22
Methyl-secodehy-droabietate	54.52								0.23
Δ6-dehydroabietane	56.32								0.04
Pimarinal	60.33							1.02	0.84
Unknown (M, 240)	61.65							4.06	1.07
Isopimarinal	62.33							0.18	0.21
Palustrinal	62.60							0.45	0.36
Palustral	62.86							0.64	0.10
Unknown (M, 288)	63.18								0.16
Dehydroabietanal	63.37							0.17	0.51
Methyl palustrate	64.62							0.38	0.19
Abietanal	65.20							0.06	0.13
Methyl dehydroabietate	66.50							0.73	0.72
Methyl abietate	68.23							0.63	0.34
Methyl callistrate	70.37							0.07	
Methyl Δ6-dehydroabietic acid	70.74								0.06
Methyl neoabietate	71.39							0.16	0.08
Methyl abietatrienoate	75.37							0.32	0.09
Total		783	294	187	201	290	405.3	237.6	64.6

pine at approximately 80 °C, where total VOC was 18 g/m³ wood (McDonald et al. 1999b). These results indicate that there is substantial variation in the measured levels of total VOC being emitted from kilns.

The total amount of VOC liberated from the kiln was significantly higher (two to three fold) than those accounted for from the difference in VOC levels between green and dried timber (Table 3). For example, β-pinene released as kiln emissions was calculated at 251 g/m³ wood and the amount of steam distillable β-pinene in the (green–dried) timber was 132 g/m³. The underestimation of the levels of monoterpenes in green wood compared to those released during kiln drying is likely due to the loss of VOC during wood sampling, variability of wood, and preparation (removal of knots and resin pockets and partial drying of the wood sample). Furthermore, consideration should be given to factors that may influence monoterpene concentrations in wood, such as site where trees are grown, age of logs from harvest, the effects of log storage and sub-sampling approach.

Emission rates of major monterpenes, α-pinene, β-pinene, limonene, α-terpinolene, α-terpineol, and total VOC during kiln drying as a function of time are shown in Fig. 8. This shows that emission rates decreased dramatically within the first ten hours of drying and that decreases in VOC emissions with time follow a similar trend as the drying curve presented earlier.

With regards to VOC, the issue of greatest environmental interest is their potential role in the formation of photooxidants such as ozone (Harley and Cass 1994).
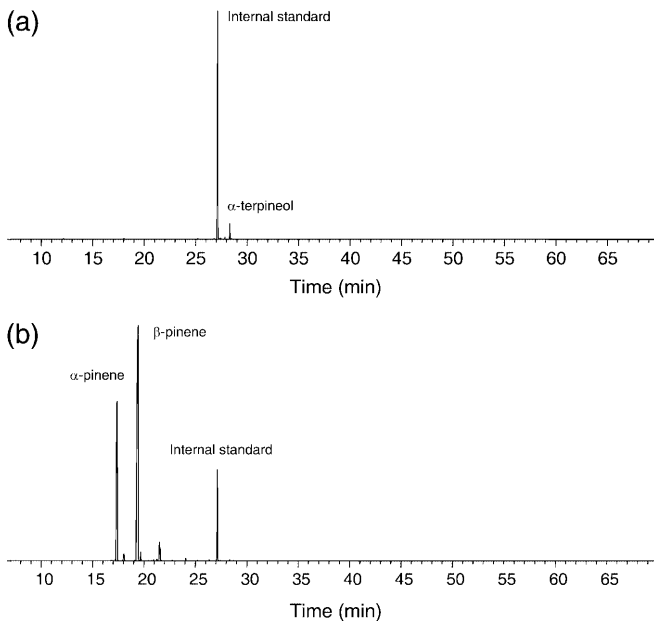
Fig. 7a, b. Total ion GC-MS chromatograms characterising **(a)** semi-volatile fraction from sampling period II and **(b)** VOC charcoal trap fraction from sampling period II, during kiln drying of radiata pine wood
Bild 7a, b. GC-MS-Chromatogramm von Abluftproben während des Trocknens von *P. radiata*: **(a)** halbflüchtige Fraktion der Probennahme II; **(b)** VOC der an Aktivkohle gebundenen Fraktion
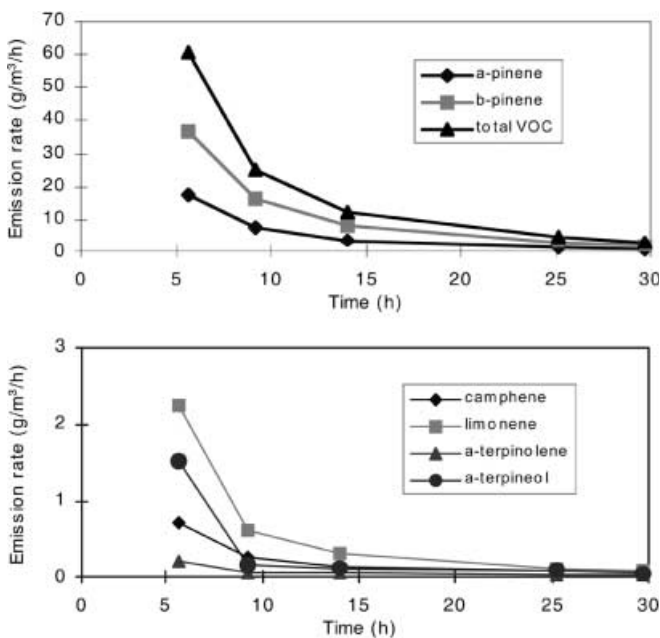
Fig. 8. Rate of (top) α-pinene, β-pinene, and total VOCs and (bottom) camphene, limonene, α-terpinolene, and α-terpineol released (g/m³ wood/h) during kiln drying of radiata pine at 100/70 °C in a commercial kiln
Bild 8. Anteil an freigesetztem α-Pinen, β-Pinen und Gesamt-VOC (oben) sowie an Kampher, Limonen, α-Terpinolen und α-Terpineol (unten), jeweils in mg/m³ Holz, während des Trocknens von *P. radiata* in einem kommerziellen Trockner

Ozone is regarded as an atmospheric pollutant since it is a strong oxidant and is believed to have caused widespread damage to forests in Europe and North America. However, there are a number of secondary competing reactions between ozone and VOC compounds which can cause the formation of other organic substances or blue haze (Atkinson 1984; Grosjean et al. 1992). Although VOC have been identified has potential contributors to atmospheric ozone, there has been considerable international debate about the relative roles of anthropogenic (man made) and biogenic (natural) sources (from plants). Current evidence suggests that both sources will need to be considered in developing effective ozone and smog reduction programmes in the Northern Hemisphere (Chameides et al. 1988).

Furfural was observed in emissions, but only during the latter part of drying. This component is a potential toxicant and has a WES-TWA of 7.9 mg/m³ air. The concentration of furfural in kiln emissions was substantially lower than the WES-TWA value.

4
Conclusions

The emissions arising from industrially drying radiata pine lumber was assessed after sampling the kiln atmosphere during drying in conjunction with determining the drying rate from air flow and temperature measurements. Monoterpenes were the predominant group of compounds emitted, and of these α-pinene and β-pinene were the two major components. Other important components emitted were ethanol, methanol, formic acid and acetic acid. Chemical emissions from the kiln were greatest during the initial part of drying. For most compound classes, the highest emission rates were found during the first 10 h. In the case of acetic and formic acids, emissions rates peaked after 25 h. Formaldehyde concentration was shown to increase at the end of drying and total formaldehyde emissions, as indicated from this study are unlikely to cause adverse environmental effects, though consideration should be given to the volume of lumber being processed and local air dispersion characteristics.

A comparison between results for total monoterpenes found in the kiln atmosphere with the total steam distillable components in green and dry wood indicated that there was a discrepancy of 2- to 3-fold in favour of the measured value for the emissions. In order to improve the mass balance for the monoterpenes, more thorough sampling of the green and dried lumber and kiln atmosphere during the drying run is required. For future studies on emissions at industrial kiln facilities, more intensive sampling will be used, especially during the early phase of drying. This study has provided substantial data on the chemical composition of emissions expected from an industrial kiln. These data can be used to undertake preliminary assessments of potential environmental impacts for new kiln installations and can be used to model potential downwind environmental effects. However, where this data is used for these purposes, it must be recognised that it was derived using specific drying conditions.

References

Atkinson R (1984) Kinetics and mechanisms of gas phase reactions of ozone with organic compounds under atmospheric conditions. Chemical Review 84:437–480

Banerjee S, Hutten M, Su W (1995) Release of water and volatile organics from wood drying. Environmental Science and Technology 29 (4):1135–1136

Burdon RD, Gaskin RE, Low CB, Zabkiewicz JA (1992) Clonal repeatability of monoterpene composition of cortical oleoresin of *Pinus radiata*. New Zealand Journal of Forestry Science 22:299–305

Chameides WL, Lindsay RW, Richardson J, Kiang CS (1988) The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. Science 241:1473–1475

Cronn DR, Truitt SG, Campbell MJ (1983) Chemical characterisation of plywood veneer dryer emissions. Atmospheric Environment 7:201–211

EPA method 0011 (1990) Method for sampling for aldehyde and ketone emissions from stationary sources, "Methods Manual for Complience with BIF Regulations," Part 266, Appendix IX, Section 3.5, EPA/530-SW-91-010

Faust B (1994) Photochemistry of clouds, fogs and aerosols. Environmental Science and Technology 28(5):217A–222A

Grosjean D, Williams EL, Seinfeld JH (1992) Atmospheric oxidation of selected terpenes and related carbonyls: gas phase carbonyl products. Environmental Science and Technology 26(8):1526–1533

Harley RA, Cass GR (1994) Modelling the concentration of gas-phase organic air pollutants: Direct emissions and atmospheric formation. Environmental Science and Technology 28(1):88–98

Ingram Jr LL, Shmulsky R, Dalton AT, Taylor FW, Templeton MC (2000) The measurement of volatile organic emissions from drying southern pine lumber in a laboratory-scale kiln. Forest Prod. J. 50(4):91–94

Kininmonth JA, Miller W, Riley S (1980) Energy consumption in wood drying. In Proceedings of the IUFRO Conference, Division V, (April) Oxford, England

Kosik M, Herain J, Domansky R (1968) Pyrolysis of beech wood at low temperatures. IV. Basic views on the formation of volatile products. Holzforschung Holzverwertung 20:56–59

Lindberg B, Rosell KG (1974) Hydrolysis and migration of O-acetyl groups during the preparation of chlorite holocellulose. Svensk Papperstidning 77:286

Lippmann M (1991) Health effects of tropospheric ozone. Environmental Science and Technology 25(12):1954–1962

Marutzky VR, Roffael E (1977) On the formaldehyde liberation by drying of wood chips. Holzforschung 31:8–12

McDonald AG, Wastney S (1995) Analysis of volatile emissions from kiln drying of radiata pine. In Proceedings of the 8th International Symposium of Wood and Pulping Chemistry. Helsinki, June 6–9, Vol III, pp 431–436

McDonald AG, Steward D, Franich RA (1999a) Monoterpene composition of radiata pine (*Pinus radiata* D.Don) sapwood from a 13 year old progeny trial. Holz Roh- Werkstoff 57:301–302

McDonald AG, Gifford JS, Dare PH, Steward D (1999b) Characterisation of the condensate generated from vacuum-drying of radiata pine wood. Holz Roh- Werkstoff 57:251–258

MFE (1994) Ambient air quality guidelines. Published by the Ministry for the Environment, Wellington, New Zealand, p 41

NCASI (1983) A study of organic compound emissions from veneer dryers and means of their control. Technical Bulletin No. 405

NCASI (1994) Volatile emissions from pulp and paper mill sources, Part X – test methods, quality assurance/quality control procedures and data analysis protocols. Method 8315. Technical Bulletin No. 684

NCASI (1996) A small-scale study on method 25A measurements of volatile organic compound emissions from lumber drying. Technical Bulletin No. 718

OSH (1994) Department of Labour, Occupational Safety and Health Service 1994: "Workplace Exposure Standards Effective from 1994", Wellington, New Zealand

Perry RH, Green D (1984) Perry's chemical engineers handbook, 6th edition, McGraw-Hill, Singapore

Rice RW (1995) Assessing human health and environmental effects related to drying wood. In: Measuring and controlling volatile organic compounds and particulate emissions from wood processing operations and wood-based products. Forest Products Society, 2801 Marshall Court, Madison, WI, USA, pp 14–16

Shmulsky R (2000a) Influence of lumber dimensions on VOC emissions from kiln-drying loblolly pine lumber. Forest Prod. J. 50(3):63–66

Shmulsky R (2000b) Influence of drying schedule on VOC emissions from kiln-drying loblolly pine lumber. Forest Prod. J. 50(4):45–48

Shmulsky R (2000c) End-grain influence on VOC emissions from kiln-drying loblolly pine lumber. Forest Prod. J. 50(5):21–23

Smelstorius JA (1974) Chemical composition of wood of Australian-grown *Pinus radiata* D. Don II. Polysaccharides. Holzforschung 28(2):67–73

Shottafer JE, Shuler CE (1974) Estimating heat consumption in kiln drying lumber. Life Science and Agricultural Experiment Station, Technical Bulletin 73, University of Maine, Orono

Word DH, Larson LJ, Law RW (1998). Preliminary results from laboratory and field studies of total hydrocarbon (VOC) analyzers and discussion of the application of method 25A measurement systems to wood product sources. In Proceedings of TAPPI International Environmental Conference and Exhibit, Vancouver, April 5–8, pp 965–981