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Research Article

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Effects of the antioxidants on the aldehyde emissions from MDF made of Scots pine (*Pinus sylvestris* L.)

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ABSTRACT

The purpose of this research was to investigate five antioxidants added to Scots pine (Pinus sylvestris L.) fiber before hot pressing in order to reduce aldehyde emissions in order to avoid the oxidation of unsaturated fatty acids during medium density fiberboard (MDF) production. Panels were produced with these fibers by means of a laboratory press. Aldehydes and other volatile organic compounds (VOCs) emissions of these boards were characterized for a period of 28 days in environmental test chambers employing Tenax-TDS/GC/MS analytics. The ability of five antioxidants to reduce aldehyde emissions was examined, and the results were compared with the emissions from control panels. Almost all of antioxidants (except ethylenediaminetetraacetic acid (EDTA) provided high reductions of total aldehyde emissions (72%-90% after 3 days). A high amount of butylatedhydroxytoluene (BHT) and butylatedhydroxyanisole (BHA) were detected on the 28 days. Dilaurylthiodipropionate (DLTP) and tertiary-butylhydroquinone (TBHQ) were the best antioxidants considering the adverse effect on other VOCs.

Key words: Aldehydes reduction; Volatile organic compounds; *Pinus sylvestris* L.; TBHQ; DLTP; BHA; BHT; EDTA; Unsaturated fatty acid; Antoxidant.

INTRODUCTION

Medium density fiberboard (MDF) made of Scots pine (*Pinus sylvestris* L.) emits several volatile organic compounds (VOCs), mainly short chain aldehydes and terpenes. Pinewood contains a number of terpenes such as α-pinene, β-pinene and 3-carene. Aldehydes arise from the degradation of unsaturated fatty acid and are formed by the autoxidation of unsaturated fatty acids after the manufacturing of the wood-based panels [1]. This theory is approved by numerous studies although it cannot be confirmed on the basis of actual studies [2-5].

The oxidation of unsaturated fatty acids is an autocatalytic process that consists of initiation, propagation, and termination. Hydroperoxides (ROOH), which are the unstable primary products formed by the propagation reaction, split into volatile aldehydes [6], [7]. The main aldehyde formed is hexanal. The dry wood of Scots pine and Norway spruce (Piceaabies) contains 3% to 5% of fatty acid triglycerides (mainly in sapwood) and resin acids (predominantly in heartwood), which comprise high levels of unsaturated fatty acids that are prone to oxidation, thus forming volatile aldehydes [1], [4]. Unsaturated oleic, linoleic, and pinolenic acids are the major components of the fatty acids in Scots pine sapwood. The predominant unsaturated fatty acid in Scots pine is reported to be oleic acid, followed by linoleic and linolenic acids [8]. Saturated aldehydes ranging from heptanal to decanal are typical degradation products of oleic acid, whereas linoleic acid mainly forms hexanal. Unsaturated compounds, such as 2,4-heptadienal, result from the oxidation of linolenic acid [9], [10], [1].

Wood based panels, especially MDF, are major sources for elevated volatile organic compound (VOC) concentrations in indoor air according to numerous studies (Jarnstrom and Saarela 2003). Aldehydes and terpenes are identified as major sources of VOCs in indoor air [11]. To increase the energy efficiency of buildings, air exchange rates in buildings have decreased, which allows VOCs emitted from building materials to accumulate. Information on the potential health hazards associated with aldehyde emissions from pine wood panels is sparse in the scientific literature. Hexanal associated with pine panels has low odor thresholds that irritate the mucous membranes and the skin. Exposure to 10 ppm hexanal will result in ocular and nasal discomfort as well as in headaches [12]. Unsaturated aldehydes are particularly irritating. For example, the α- and β-unsaturated aldehydes, such as 2-heptenal and 2-octenal, induce genotoxic effects at exposure concentrations of up to 100 mg/m3 and 40 mg/m3, respectively [13]. High levels of volatile aldehydes emitted from Scots pine products are responsible for their pungent smell, which leads to consumer dissatisfaction [8].

The aim of this research is to investigate the ability of five antioxidants to reduce aldehyde emissions by preventing the degradation of unsaturated fatty acids in softwood resin to reduce and control potential indoor emission sources. MDF panels added with antioxidants were manufactured in a laboratory. The aldehyde and other VOCs emissions emitted from the boards were then measured.

EXPERIMENTAL SECTION

Materials: TBHQ (97%), DLTP (with less than 3% dodecanol, 97.5%), BHA (98.5%), BHT (99%) and EDTA (99%) in powder form were purchased from Sigma-Aldrich Corporation, USA. Urea formaldehyde (UF) resin (batch number: 337; solid content: 68%, density: 1.3 g/cm3, pH: 7.6, viscosity: 320 mPa.s at 20°C) was supplied by BASF-The Chemical Company, Germany.

Industrial Scots pine fibers was utilized as raw material for the tested boards. The MDF panels were manufactured in the laboratory of the Thuenen Institute of Wood Research (TI), Hamburg, Germany. Antioxidants were added to fibers (dried to moisture to 2-3%) while blending with 12% UF resin, respectively. And then, a mat was formed and hot pressed for 10 s per 1 mm panel thickness at a temperature of 220 °C. MDF thickness was 9 mm and target density was 700 kg/m^3. Under this condition, one percent (dry fiber basis) of TBHQ, DLTP, BHA, BHT and 0.5% of EDTA panels were produced.

Methods: After cooling to ambient temperature, MDF panels were cut into 21 cm by 21 cm size from the center of the board. Aluminum-coated adhesive tape was used to seal the edges to prevent edge emissions. Overlapping 1 cm, sample was leaded an emission area of 722 cm^2. The samples were then placed in an environmental testing chamber to start the emission testing process. The test specimens remained inside the chamber during this process.

Sampling and analytical procedures as well as the equipment were adopted for the ISO 16000-6:2011 [14]. Testing boards were placed in environmental test chambers (vacuum glass desiccators) with a volume of 23L. A constant airflow (1.2L min^{-1}) was led through the chamber to obtain an air exchange rate of 3.1 h^{-1}. The loading factor was set to 3.1 m^{2}m^{-3} according to an area specific airflow rate of 1.0 m3m^{-2}h^{-1}. The airflow was conditioned for a temperature of 23°C and 50% relative humidity, both measured at the inlet port of the chamber.

Air samples were collected with Tenax TA (200 ng, 60 meshes to 80 meshes) tubes by using a sampling pump with an electronic flow controller. A sample flow rate of 100 ml min-1 was used to give a total air volume of 2 to 3l. Before sampling, each tube was spiked with 200 ng toluene$_{d8}$ dissolved in methanol as the internal standard.

After sampling, the tubes were thermally desorbed in a TDS 3 (Gerstel, Muelheima.d. Ruhr, Germany). And then, Gas chromatography (GC) with mass spectrometry (MS) was performed on an Agilent 6895/5973N GC/MS system (Agilent Technologies, California, USA). Quantification was achieved through multipoint calibration with reference compounds. Detected peak areas were multiplied with the relative response factors of the internal standard.

The thermal desorption conditions were as follows: desorption temperature, 280 °C; desorption time, 7 min; cold trap low temperature, -15 °C; and split flow, 22mL/min (split ratio 19.3:1.0). A 30 m analytical column (1701ms, film 0.25 µm, i.d. 0.25 mm; Agilent Technologies, California, USA) was used. The GC temperature program was set to an initial value of 32 °C, which was maintained for 3 min, ramped to 90 °C at 6 °C min^{-1} for 4 min, increased at 8 °C min^{-1} to 200 °C, and finally, increased at 12 °C min^{-1} to 240 °C, which was maintained for 2 min. The MS detector operated with 2.2 scans s^{-1} (29 amu to 300 amu) at an interface temperature of 280 °C.

Table 1 The lead compounds of VOC emissions from MDF by adding different antioxidants

	3 days						14 days						28days					
Compounds	Ctrl	EDTA	DLTP	TBHQ	BHT	BHA	Ctrl	EDTA	DLTP	TBHQ	BHT	BHA	Ctrl	EDTA	DLTP	TBHQ	BHT	BHA
Aldehydes																		
Pentanal	4	2	ND	ND	ND	ND	6	3	ND	ND	ND	ND	6	2	ND	ND	ND	ND
Hexanal	18	10	9	4	3	4	33	16	3	2	2	2	42	13	1	1	1	2
Benzaldehyde	3	2	3	2	4	2	3	2	1	ND	ND	ND	4	2	ND	ND	ND	ND
Furfural	10	8	8	9	13	8	3	4	3	3	5	4	3	2	1	2	3	2
Nonanal	4	2	2	2	2	2	2	1	ND	ND	ND	ND	3	1	ND	ND	ND	ND
Other aldehydes	6	2	2	ND	1	1	7	2	2	ND	ND	ND	11	1	ND	ND	ND	ND
Terpenes																		
α-Pinene	2	3	3	5	3	4	ND	1	ND	1	1	1	1	ND	ND	ND	ND	ND
3-Carene	1	1	1	2	2	2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Terpineol	147	151	216	220	272	195	12	21	36	31	40	38	5	4	6	7	9	9
Other terpenes	10	9	14	18	39	10	ND	ND	ND	ND	18	ND	ND	ND	ND	ND	21	ND
Others						ND	ND	ND				ND	ND	ND				ND
Dodecanol	ND	ND	60	ND	ND	ND	ND	ND	74	ND	ND	ND	ND	ND	45	ND	ND	ND
2-hexanol	13	15	11	22	19	17	ND	ND	ND	1	1	1	ND	ND	ND	ND	ND	ND
Acetic acid	427	331	339	326	390	313	136	159	152	136	152	151	65	80	49	96	96	98
Hexanoic acid	5	3	3	6	3	4	5	4	2	ND	ND	1	14	3	ND	ND	ND	ND
Σaldehydes	45	26	24	16	23	17	53	27	9	5	7	6	71	21	3	4	4	4
Σterpenes	160	163	234	240	316	211	12	22	36	32	59	39	6	4	6	7	30	9
∑VOC	670	563	694	642	792	604	207	214	275	179	225	207	159	108	102	106	132	114
DLTP	ND	ND	12	ND	ND	ND	ND	ND	8	ND	ND	ND	ND	ND	4	ND	ND	ND
TBHQ	ND	ND	ND	36	ND	ND	ND	ND	ND	25	ND	ND	ND	ND	ND	19	ND	ND
BHT	ND	ND	ND	15	7365	5	ND	ND	ND	4	4887	ND	ND	ND	ND	3	5510	ND
BHA	ND	ND	ND	ND	1	1315	ND	ND	ND	ND	ND	1291	ND	ND	ND	ND	ND	1198

ND = Not detected

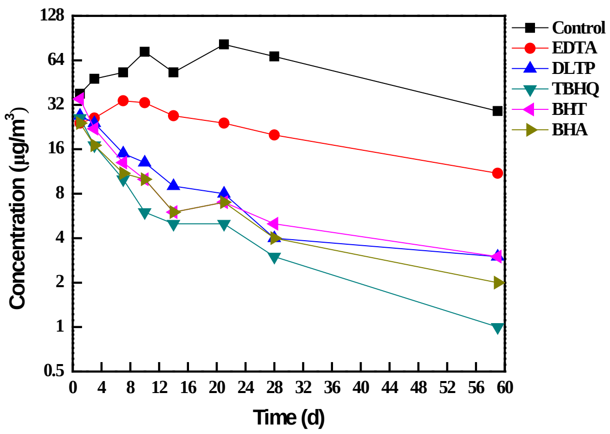

Fig. 1 Total aldehyde concentration from MDF treated with different antioxidants

The oxidation of unsaturated fatty acids was an autocatalytic process that consists of initiation, propagation, and termination [6], [7]. Antioxidants of BHA, BHT and TBHQ were classified primary antioxidants as well as phenolics antioxidants, because they acted as free radical scavengers and inhibited the initiation step [17]. The primary antioxidants reacted with peroxy radicals (ROO·) and converted them to more stable, nonradical products. These antioxidants were capable to donating a hydrogen atom to lipid radicals and produced lipid derivatives, which were more stable and less readily available to participate in propagation reactions. This might be the reason why their effective on aldehyde reduction were similar. The common feature of these antioxidants was that they were mono- or polyhydroxy phenols with various ring substitutes (Fig. 2). As substitution with butyl or ethyl group/s para to the hydroxyl groups also enhances the antioxidant activity [18], [19]. Thus, TBHQ was the most effective antioxidants on aldehyde emissions through against the oxidant of unsaturated fatty acids contained in pine.

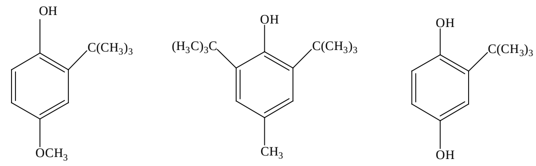

Fig. 2 Chemical structures of synthetic phenolic antioxidants

DLTP was classified as secondary antioxidants as well as classⅡ antioxidants. DLTP acted to decompose ROOH into nonradical species, prolonging the initiation period before oxidation, according to well-recognized antioxidant mechanism. DLTP, as a familiar sulfur antioxidant, was oxidized into sulfoxides, which had higher antioxidant activities than the original sulfur compounds. Through further reactions with ROOH, the sulfoxides were converted into sulfones that had no antioxidant properties [17]. Therefore, DLTP behaved as a preventive antioxidant by inhibiting autocatalytic action and less effect than phenolics antioxidants (Fig.1).

Aside from the auto-oxidative reaction, unsaturated fatty acids also underwent spontaneous peroxidation to produce a trace of hydroperoxides ROOH, which could lead to an initiation reaction of oxidation through the action of a hemolytic cleavage. Moreover, the metals contained in wood (i.e., Fe, Mn, and Cu), as well as the high temperatures of drying and hot pressing were probably sufficient for an initiation reaction. EDTA was commonly used in extending the shelf life of lipid because of their metal chelating properties. The activity of EDTA depended on pH and the presence of other chelatable ions (e.g., Ca) as well as the ability of hydrolysis [20], which may explain that EDTA was the last effect on aldehyde reduction by inhibiting lipid's oxidant activity.

Nonaldehyde VOCs: Aldehydes emissions were mainly composed of hexanal and pentanal as well as smaller amounts of other saturated and unsaturated compounds such as heptanal and 2-octenal. Beside aldehydes, large amounts of other substances are measurable, such as terpenes, organic acids and alcohols. Terpineol and acetic acid were the most abundant; these compounds accounted for 68% (Control), 95% (EDTA), 59% (DLTP), 90% (TBHQ), 79% (BHT), and 89% (BHA) on the 28 days. The detected composition as well as the course of emissions was similar to results of other researchers [2], [15], [21].

Terpenes emissions from all panels treated with antioxidants increased during the test period compared with emissions from the control panel. Nonetheless, almost all of the antioxidants (except EDTA) were detected during the test periods. The emission of BHT was kept almost still during the testing time, while BHA was decreased with time. On day 28, 4 (DLTP), 19 (TBHQ), 1198 (BHA), and 5510 μg/m^3 (BHT) were released. On the whole, DLTP and TBHQ were the most effective antioxidants to control aldehyde emissions for this batch of fibers.

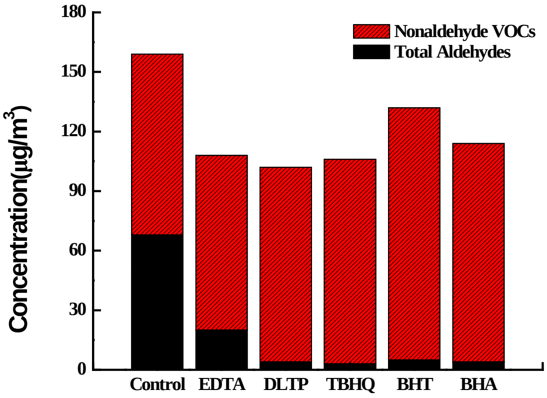

Fig. 3. Aldehydes and nonaldehyde VOCs (except antioxidants) emissions for each manufactured MDF treated with five antioxidants
Measurements were made after samples had been in the chamber for 28 days

CONCLUSION

Five antioxidants, besides their application as antioxidants in food and animal feeds, appeared to be promising candidates to remove aldehyde emissions from Scots pine MDF, probably through the antiautoxidation of unsaturated fatty acids. A conclusion could be drawn that total aldehyde concentration emission from MDF panels produced with UF resin that contained either antioxidants decreased compared with that from the control MDF panels. By considering economic and environmental factors, DLTP and TBHQ were the most suitable additional amounts to reduce the stack of Scots pine MDF.

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