Chemical Composition and Efficiency of Bio-oil Obtained from Giant Cane (*Arundo donax* L.) as a Wood Preservative

Ali Temiz,[a,*] Selcuk Akbas,[b] Dmitri Panov,[c] Nasko Terziev,[d] M. Hakkı Alma,[e] Salih Parlak,[f] and Gaye Kose [a]

This study aimed at determining the chemical composition of bio-oil from giant cane (*Arundo donax* L.), as well as its performance as a wood preservative. The performance was determined through water absorption, tangential swelling, and resistance to fungi and termites. Bio-oil was obtained by pyrolysis at 450 to 525 ºC. The yield of liquid, char, and gas was determined to be 45, 30, and 25%, respectively. The most abundant chemical compounds found in the bio-oil were acids, ketones, furans, benzenes, phenols, sugars, and guaiacols. Scots pine sapwood was impregnated with the obtained bio-oil at concentrations of 10 and 20%. Additionally, treated samples were impregnated with epoxidized linseed oil to study its effect on bio-oil leachability. The retention of the giant cane bio-oil was in the range of 50 to 100 kg m^{-3}. Leached samples were exposed to white- and brown-rot fungi, according to European standard EN 113. Wood impregnated with only cane oil demonstrated a durability that classifies the treatment as very effective (mass loss less than 3%). Epoxidized linseed oil treatment significantly reduced water absorption of the treated samples with bio-oil and further improved the durability. A termite test showed that bio-oil was also effective against *Reticulitermes flavipes*.

Keywords: Decay and termite resistance; Giant cane; Pyrolysis; Scots pine; Water absorption

*Contact information: a: Karadeniz Technical University, Faculty of Forestry, 61080 Trabzon, Turkey; b: Artvin Coruh University, Faculty of Forestry, 08000 Artvin, Turkey; c: University of Tartu, Institute of Chemistry, Department of Nature and Technology, Estonia; d: Swedish University of Agricultural Sciences, P.O. Box 7008, SE-750 07 Uppsala, Sweden; e: Kahramanmaras Sutcu Imam University, Faculty of Forestry, 46060, K. Maras, Turkey; f: Aegean Forest Research Institute, 35315, Urla, İzmir, Turkey; *Corresponding author: temiz@ktu.edu.tr*

INTRODUCTION

Wood is a natural, renewable engineering material with unique properties that facilitate its use for indoor and outdoor applications. However, due to some undesirable properties, such as susceptibility to biodegradation when exposed to microbiological attack and dimensional instability under varying moisture conditions, wood has a limited service life (Mohan *et al.* 2008; Temiz *et al.* 2010). In order to extend the service life of unprotected wood, chemical treatments, mainly water- and oil-based preservatives, are widely used. The most common wood preservatives are the oil-based preservatives creosote and pentachlorophenol and the water-based preservatives chromated copper arsenate (CCA), amine copper quat (ACQ), and amine copper azole (CA). Increasing public concern about the use of arsenic has led to the restriction or ban of chromium- and arsenic-containing preservatives in the EU countries and the US (Gezer *et al.* 2005;

Temiz *et al.* 2007; Mohan *et al.* 2008). Furthermore, copper-containing formulations have a high aquatic toxicity, introducing further environmental concern in addition to Cr and As (Temiz *et al.* 2007).

Biomass represents the cheapest and most abundant feedstock available in large volume. Approximately 117 billion tons (based on the oven dry material) of plant biomass, including by 80 billion tons in forests biomass is produced in the world annually (Dobele *et al.* 2007; Temiz *et al.* 2010). Interest in using biomass for bioenergy is increasing worldwide. Most of the common processes that convert biomass to liquid fuels begin with pyrolysis. Pyrolysis is a term that describes the degradation of macromolecular materials using heat under anaerobic (without oxygen) conditions (Meier and Faix 1999; Mohan *et al.* 2006). The pyrolytic breakdown of biomass produces solid substances, liquid, and gas; the relative amounts of the three fractions formed depends on the process variables (Mohan *et al.* 2006). Bio-oils extracted by pyrolysis are formed by rapid and simultaneous de-polymerization of cellulose, hemicelluloses, and lignin. The bio-oils are a mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, carboxylic acid, hydroxyaldehydes, hydroxyketones, sugars, and phenolics (Temiz *et al.* 2010). Because of their complex structure, it is presumed that bio-oils can protect wood against fungi and insect degradation. Bio-oil can be considered as an alternative to creosote. In contrast to creosote, bio-oil does not contain polynuclear aromatic hydrocarbons (PAH). It does contain many phenolic compounds that are effective against decay fungi. PAH are dangerous pollutants, affecting the environment and humans' health, in addition to acting as irritants (Gallego *et al.* 2008). Furthermore, bio-oils are composed of biodegradable compounds. Some studies have been conducted on the use of pyrolysis oil for wood preservation (Kartal *et al.* 2004; Mansoor and Ali 1992; Mazela 2007; Meier *et al.* 2001; Mourant *et al.* 2005; Mourant *et al.* 2007; Temiz *et al.* 2010). However, the main drawback of impregnated bio-oils is their leachability from wood (Mohan *et al.* 2008; Temiz *et al.* 2010).

The objectives of the present study were to determine the chemical composition, hydrophobic properties, decay, and termite resistance of Scots pine wood treated with bio-oil obtained from giant cane (*Arundo donax* L.) pyrolysis and to study a method for reducing its leachability by means of epoxidized linseed oil.

EXPERIMENTAL

Pyrolysis Process

Giant cane (*Arundo donax*) samples with a moisture content of 6.5% (based on oven-dry weight) were obtained from the western part of Turkey (38° 21' 3.43" longitude and 26° 48' 39.15" latitude) and used for a pyrolysis process that was carried out in a fixed bed reactor type pyrolyzer (Ø 8 cm, 35 cm length, and power of 2 kW), as shown in Fig. 1. The process was carried out at 450 to 525 °C for 30 min in an inert gas (N_2) with a constant flow rate of 100 mL min^{-1} by using a heating rate of 10 °C min^{-1}. The inert gas minimized secondary reactions (such as thermal cracking, re-polymerization, and re-condensation) and maximized the liquid yield. Liquid fractions (bio-oil and water) obtained from the pyrolysis process were collected in a condenser (maintained at 0 to 5 °C) and washed by dichloromethane. The aqueous phase was separated from the oil by

using a separatory funnel and weighed to calculate product yields. A rotary evaporator was used to remove the remaining water.

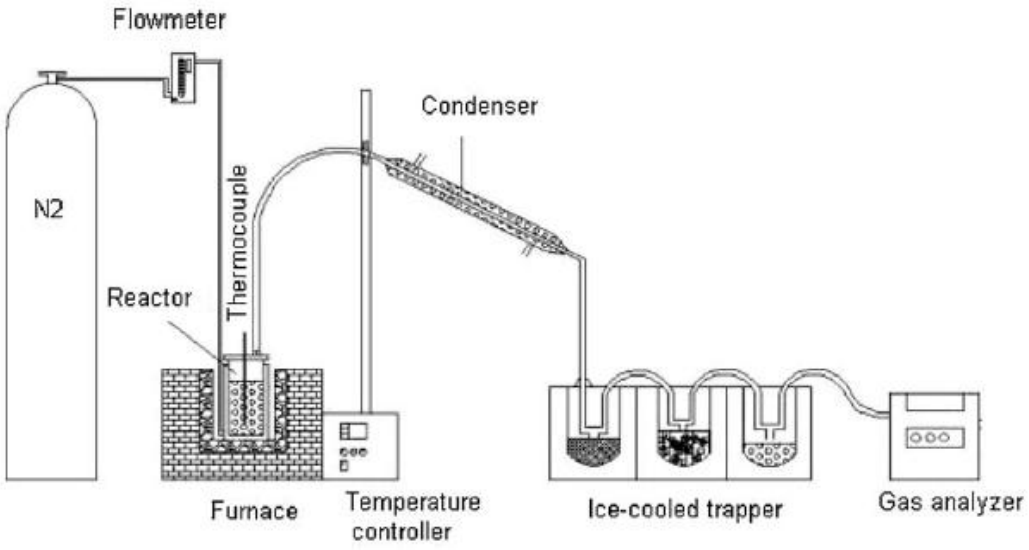

Fig. 1. Experimental set-up of fixed bed reactor type pyrolyzer

Chemical Composition of Giant Cane

The raw material was analyzed for holocellulose, α-cellulose, lignin, ash, alcohol-benzene, cold and hot water, and 1% sodium hydroxide solubility according to TAPPI standard methods T-203-0S-61, T-222, T-221, T-204, T-257, and T-212 (1992). The amount of sugar (cellobiose, rhamnose, mannose, arabinose, galactose, xylose, and glucose) in giant cane was determined according to the method described by Ucar and Balaban (2003).

Elemental Analyses and Chemical Composition of Bio-oil

Water content, viscosity, and pH

Elemental analyses of carbon (C), oxygen (O), hydrogen (H), and nitrogen (N) were performed by a CHNS Flash 1112 L thermoelectron instrument. The process (using 3 mg of bio-oil) was carried out at 950 to 1000 °C. The amount of water in the bio-oil was determined according to ASTM D1744 standard using the "MKC 501 D" Karl Fischer titration method. Viscosity was measured according to standard DIN 51562. The pH of the bio-oil was also determined.

Gel permeation chromatography (GPC) analysis of bio-oil

Gel permeation chromatography is a chromatographic method in which particles are separated based on their size, *i.e.*, hydrodynamic volume. In this study, GPC was used to determine the average molecular weight (M_w) and the number of the average molecular weight (M_n). The test was carried out at 60 °C, and 3.5 g of bio-oil was used. A rotating cylinder was used for 24 h to homogenize the solution before testing. Flow rate and wavelength were adjusted to 0.800 mL min^{-1} and 254 nm, respectively. Dispersity was calculated according to Equation 1,

$$D = M_w/M_n \quad (1)$$

where D is dispersity, M_n is the number average molecular weight, and M_w is average molecular weight.

Gas chromatography/mass spectrometry (GC/MS) analysis

GC/MS analysis of the bio-oil was performed on an Agilent 6890 GC system. The chromatograph was equipped with a DB-1701 (Agilent J&W) fused-silica capillary column. The GC column used was 30 m × 0.24 mm, 0.25 μm film thickness, and Agilent 5973 mass selective detector (EI at 70 eV, ion source temp 280 °C). The injector temperature and pressure were 250 °C and 226 Nm^{-2}, respectively. The temperature of MS started at 45 °C and was increased 3 °C min^{-1} to 280 °C.

Preparation of Epoxidized Linseed Oil (ELO) and Treatment of Wood Samples

The method for preparation of ELO was described by Panov *et al.* (2010), where linseed oil and hydrogene peroxide were used. Acetic acid was added as a catalyst to open the epoxy rings.

Scots pine sapwood (*Pinus sylvestris* L.) samples (15 × 20 × 50 mm^3) were treated with the obtained giant cane bio-oil by full cell treatment. The samples were treated with 10 and 20% solutions of bio-oil diluted with ethanol. In an additional impregnation, the samples primarily treated with 10 and 20% solutions of bio-oil were secondarily impregnated with ELO, which was applied using the empty cell process for fixation of the bio-oil into the wood cell wall. The full cell impregnation procedure consisted of 10 min vacuum (65%) and 20 min pressure (100 MPa), whereas the empty cell procedure consisted of 20 min pre-pressure (125 kPa) and after the period of preliminary air pressure, ELO is forced to into the cylinder and 50 min pressure (250 kPa) and 5 min of final vacuum. After the treatment, the samples were removed from the autoclave and weighed to determine the retention of oil (Table 4 and 6). All samples were dried at 65 °C for 24 h.

Leaching, Water Absorption (WA), and Tangential Swelling Tests (TST)

Prior to the decay test, all treated Scots pine samples (15 × 25 × 50 mm^3) were leached in deionised water according to the American Wood Protection Association (AWPA) standard E11 (2008) to obtain an estimate of the leaching effect that would eventually occur in service. The water was replaced with fresh deionized water after 6 h, 1 day, 2 days, and then every 2 days thereafter for a total of 14 days. The collected water was analyzed using GC/MS and used for a fungal inhibition test.

Additional treated samples (6.4 × 25 × 50 mm^3) were tested according to AWPA E4 (2003). The samples were conditioned at 27 ± 2 °C and 65 ± 5% relative humidity (RH) to a constant weight before testing. Treated and untreated samples were placed into beakers filled with deionized water, which was replaced with fresh deionised water after 15, 45, and 90 min and 3, 24, and 48 h. Weights and dimensions of the samples were recorded, and WA and TST values were calculated according to Equations 2 and 3 after each water replacement:

$$WA = [(W_2 - W_1) / W_1] \times 100 \quad (2)$$

$$TST = [(T_2 - T_1) / T_1] \times 100 \quad (3)$$

In these equations, W_1 and W_2 are the weights of the wood specimens before and after the test, T_1 is the initial tangential dimensions of the specimen, and T_2 is the tangential dimension at any given time during soaking in water.

Fungal Inhibition, Decay, and Termite Tests

Three hundred mL of solution (2% agar, 4% malt) was prepared from the collected leachates. An additional amount was prepared with distilled water as a control. One white rot (*Trametes versicolor* CTB 863A) and three brown rot fungi (*Coniophora puteana* BAM Ebw. 15, *Gloephyllum trabeum* BAM Ebw. 109, and *Postia placenta* FPRL 280) were inoculated for the inhibition test. The Petri dishes (Ø 9 cm) were exposed at 22 ± 1 °C and 70 ± 5% RH, and the myceliar growth was measured after 1 and 2 weeks of exposure.

Assessment of the treated wood durability against fungal attack by basidiomycetes was carried out according to European standard EN 113 (1996) on leached wood samples. The test used the previously mentioned white and brown rot fungi. The evaluation of the laboratory decay test was based on recorded mass loss after a fixed time period of exposure (16 weeks), as presented in Table 6.

Treated samples (15 × 25 × 25 mm^3) were exposed to termite attack by the species *Reticulitermes flavipes* (Kollar). A total of 100 workers, 1 soldier, and 5 nymphs were introduced into Petri dishes (Ø 18.5 cm) containing 25 g vermiculite. The test was carried out at 27 ± 2 °C and 80 ± 5% RH for 4 weeks. Termite mortality was monitored daily, and the mass loss of each sample was calculated (Table 7).

RESULTS AND DISCUSSION

Characterization of Bio-oil

The chemical composition of giant cane (*Arundo donax* L.) used in this study is shown in Table 1.

Table 1. Chemical Composition and Amount of Monosaccharides in Giant Cane

Substance	Average, %	Monosaccharides	Average, %
Extractives (cold water)	6.15 (0.42)*	Rhamnose	0.15 (0.01)
Extractives (hot water)	8.01 (0.14)	Mannose	0.35 (0.01)
Extractives (1% of sodium hydroxide)	29.39 (0.46)	Arabinose	2.00 (0.03)
Extractives (alcohol-benzene)	1.29 (0.11)	Galactose	0.84 (0.03)
Lignin	22.40 (1.58)	Xylose	33.88 (0.26)
Holocellulose	72.52 (0.61)	Glucose	62.13 (0.31)
Cellulose	45.12 (0.05)	4-O-Me**	0.65 (0.01)
α-cellulose	42.84 (0.66)		
Ash	2.39 (0.09)		

***** Standard deviation in parentheses
****** 4-O-methyl glucuronic acid

The giant cane showed an average of 22% lignin and 42% α-cellulose, and thus it contains somewhat less lignin than wood (24 to 34%). The cane's lignin and cellulose contents were found to be similar to those of bamboo (21 to 32% and 26 to 43%, respectively). The hemicellulose content of giant cane (27%) does not differ significantly from that of hardwoods (20-28%) and grain straw (26-32%). The carbohydrate composition in hemicellulose of giant cane showed that amount of pentosans was remarkably more predominant than hexosans. Similar results have been previously reported by several researchers (Atchison 1993; Jeon *et al.* 2010; Rydholm 1976; Shatalov *et al.* 2001).

The yields of liquid, char, and gas fractions obtained during the giant cane pyrolysis were 45, 30, and 25%, respectively. A particle size of 250 µm was used for all experiments, since the particle size significantly affects the yields of pyrolysis products. An increase in the particle size causes greater temperature gradients inside the particles, and thus the core temperature of a particle is lower than on the surface, resulting in an increase in bio-char yield and a decrease in bio-oil and gas yields (Ertas and Alma 2010; Mohan *et al.* 2006). The pyrolysis time was set to 30 min, which corresponds to the so-called "slow pyrolysis process," according to Mohan *et al.* (2006).

An increase in the heating rate from 450 to 525 °C led to a slight increase of the liquid yield. Some authors have reported that the total oil yield increases when pyrolysis temperature increases (Demirbas 2004; Gonzalez *et al.* 2005). Gonzalez *et al.* (2005) found that the maximum yield of the oil fraction was achieved at temperatures in the range of 400 to 500 °C. This justified the chosen pyrolysis temperature in the range of 450 to 525 °C. The elemental analysis showed that the bio-oil made of giant cane consisted of 65.28% carbon, 26.48% oxygen, 7.37% hydrogen, and 0.87% nitrogen. The heating value of the bio-oil was calculated as 18.64 MJ kg^{-1} using the Dulong formula (Eq. 4).

$$\text{Heating value (MJ kg}^{-1}) = 33.83(C) + 144.3(H-O/8) \quad (4)$$

Some properties that are of importance when bio-oil is used as fuel, as well as results of GPC analysis of the bio-oil, are presented in Table 2.

Table 2. Bio-oil Properties of Importance for Burning and Results of GPC Analysis

Properties	Crude bio-oil (100%)	10% solution of bio-oil
Water content (%)	3.43	9.10
Kinematic viscosity (cSt, 55 °C)	16.74	-
pH	4.05	-
	GPC analysis (g mol^{-1})	
M_w (g mol^{-1})	$5.2168e^2$	$5.1643e^2$
M_n (g mol^{-1})	$1.1961e^2$	$1.0816e^2$
$D = M_w/M_n$	$4.3617e^0$	$4.7748e^0$

It has been reported that the water content of bio-oil ranges from 15 to 30%, depending on the moisture content of the raw material and dehydration reactions during pyrolysis (Ertas and Alma 2010; Mohan *et al.* 2008). In the present study, the water content of bio-oil was 34%. The compounds identified in the giant cane bio-oil are listed in Table 3.

Table 3. Compounds Identified in Giant Cane Bio-oil

Compounds	Relative content (%)
Acids	4.64
Nonaromatic ketones	5.17
Furans	3.60
Benzenes	0.23
Phenol	1.27
Alkylphenols	4.60
Guaiacols (methoxy phenols)	7.10
Syringols (dimethoxy phenols)	5.72
Miscellaneous	0.30

The identified compounds in the bio-oil were acids, ketones, furans, benzenes, phenols, sugars, guaiacols, and multifunctional compounds. Some volatile compounds of low concentrations were not precisely determined due to complex peaks displayed on the chromatogram. In addition, the studied bio-oil contained many non-volatile compounds that are not GC-eluted (Qiang *et al.* 2008). High acetic acid content in bio-oil can be attributed to a high xylose content in giant cane. Acetic acid is formed from acetyl groups in hemicellulose (Azeez *et al.* 2010; Kartal *et al.* 2004; Mohan *et al.* 2006).

Water Absorption (WA) and Tangential Swelling Test (TST)

Water absorption (WA), tangential swelling (TST), and retention of treated wood are shown in Table 4.

Water absorption (WA) values of control groups showed an increase from 63 to 89% after 48 h of exposure in water. The control group showed significantly higher water absorption results than the studied bio-oils. The lowest water absorption results for the bio-oils studied were obtained for the samples treated with 20% bio-oil combined with ELO after 48 h exposure in water. The secondary treatment with ELO significantly reduced the WA of the samples treated with bio-oil. One possible explanation could be the presence of fatty acids in the linseed oil. Linoleic acid, one of the main acids in linseed oil, possesses a double C=C bond, which becomes very reactive when epoxidised and is able to react with the hydroxyl groups of wood.

Tangential swelling of control samples showed the highest values; that is, all treated samples demonstrated less swelling than the control samples. The secondary treatment with ELO further reduced the tangential swelling, but the effect was marginal.

Fungicidal Efficiency of Bio-oil

Analysis of leachate

Water collected from the leaching test was analyzed with GC-MS. As an example, the chromatograms of leachate obtained from samples treated with 10% solution of bio-oil and bio-oil mixed with ELO are presented in Figs. 2 and 3.

Table 4. Water Absorption, Tangential Swelling, and Retention of the Impregnated Bio-oil

Treatment	Retention (kg m^{-3})	15 min	45 min	90 min	3 h	24 h	48 h
Water Absorption (%)							
20% bio-oil + ELO	104.99 (8.01)	4.84^{a}* (1.63)**	7.79^{a} (1.7)	9.11^{a} (2.43)	12.69^{a} (2.28)	21.93^{a} (1.91)	36.78^{a} (2.47)
20% bio-oil	102.24 (3.32)	31.30^{c} (2.82)	37.98^{c} (3.89)	39.88^{c} (2.03)	43.23^{c} (2.69)	43.22^{c} (3.07)	70.82^{b} (3.18)
10% bio-oil + ELO	49.91 (1.18)	6.19^{ab} (0.93)	9.65^{ab} (1.28)	11.73^{ab} (0.95)	15.14^{ab} (1.87)	23.54^{ab} (2.65)	40.00^{a} (0.94)
10% bio-oil	48.30 (1.88)	42.22^{d} (0.73)	46.67^{d} (0.78)	48.27^{d} (0.52)	50.58^{d} (0.81)	63.17^{e} (0.94)	79.96^{c} (0.53)
Control	-	63.77^{e} (1.97)	65.39^{e} (0.37)	63.12^{e} (2.26)	63.09^{e} (2.35)	71.53^{f} (3.02)	89.94^{d} (3.83)
Tangential Swelling (%)							
20% bio-oil + ELO	104.99 (8.01)	0.47^{a}* (0.1)[1]	1.52^{a} (0.25)	2.22^{a} (0.18)	3.30^{a} (0.33)	4.94^{a} (0.19)	5.09^{ab} (0.17)
20% bio-oil	102.24 (3.32)	4.88^{c} (0.06)	5.06^{c} (0.02)	5.11^{d} (0.19)	5.08^{d} (0.19)	5.27^{b} (0.15)	5.25^{bc} (0.19)
10% bio-oil + ELO	49.91 (1.18)	0.72^{a} (0.14)	1.82^{a} (0.18)	2.80^{b} (0.23)	3.66^{b} (0.1)	4.81^{a} (0.00)	4.92^{a} (0.03)
10% bio-oil	48.30 (1.88)	5.08^{c} (0.23)	5.22^{c} (0.23)	5.23^{d} (0.26)	5.23^{d} (0.24)	5.40^{b} (0.3)	5.42^{cd} (0.31)
Control		5.75^{d} (0.15)	5.87^{d} (0.18)	5.90^{e} (0.16)	5.96^{e} (0.16)	5.99^{c} (0.18)	6.15^{e} (0.17)

***** Identical letters indicate no statistical significance
****** Standard deviation within parentheses

The number of compounds determined in the leachate from the samples treated with 10% solution of bio-oil was 74, while in the treatment with mixed oil and ELO, only 21 compounds were determined (compare Figs. 2 and 3). The comparison clearly demonstrated that the additional ELO treatment decreased bio-oil leaching from the treated wood. This was further confirmed by water absorption and decay test results. The most abundant compound found in the 10% solution of bio-oil leachate was catechol (24%), while in the combination with ELO, syringol (34%, Fig. 3) was dominant.

Fungal inhibition and decay test

Mycelium growth of leachate after 1 and 2 weeks of exposure is shown in Table 5. Regardless of the type of test fungus, no fungal growth was observed on the solutions containing ELO, while the solutions containing only bio-oil were covered to some extent with mycelia. The fungal growth on 10% solution of bio-oil was more intensive than on 20% bio-oil solution. The mycelia on the control groups (prepared with distilled water) covered a significant part (diameter of 30 to 35 mm) of the solution after 2 weeks of exposure; the entire dishes were covered with mycelia when inoculated with *T. versicolor*. The fungal inhibition test is not related to wood durability, but is shown as an argument in favour of the addition of ELO to ensure a synergic effect when mixed with cane oil. The decay resistance of the treated wood is shown in Table 6.

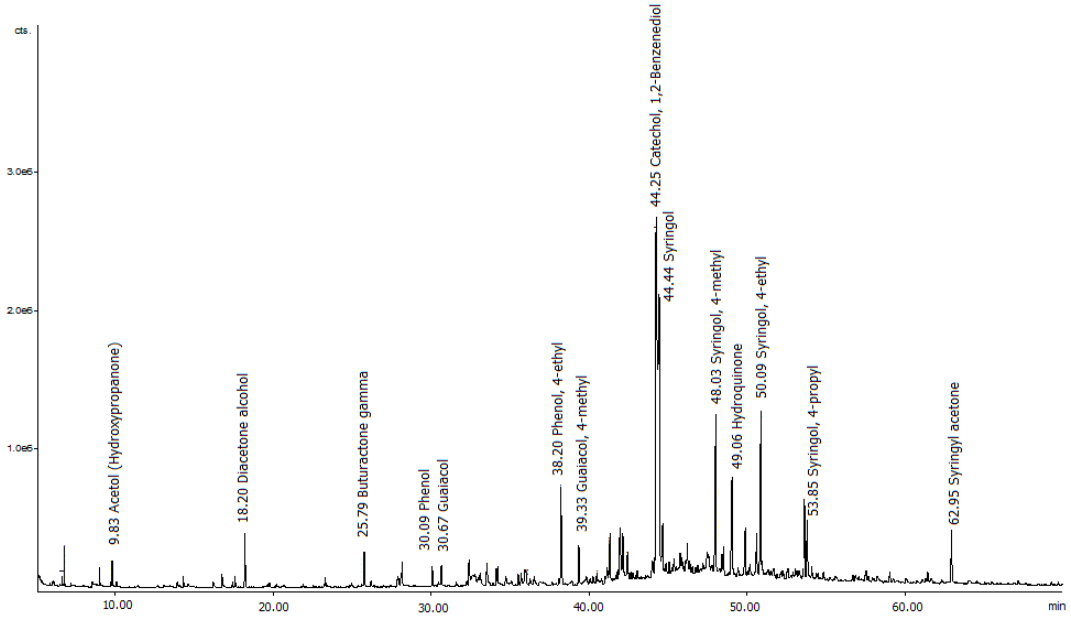

Fig. 2. The chromatograms of leachate obtained from samples treated with 10% solution of bio-oil

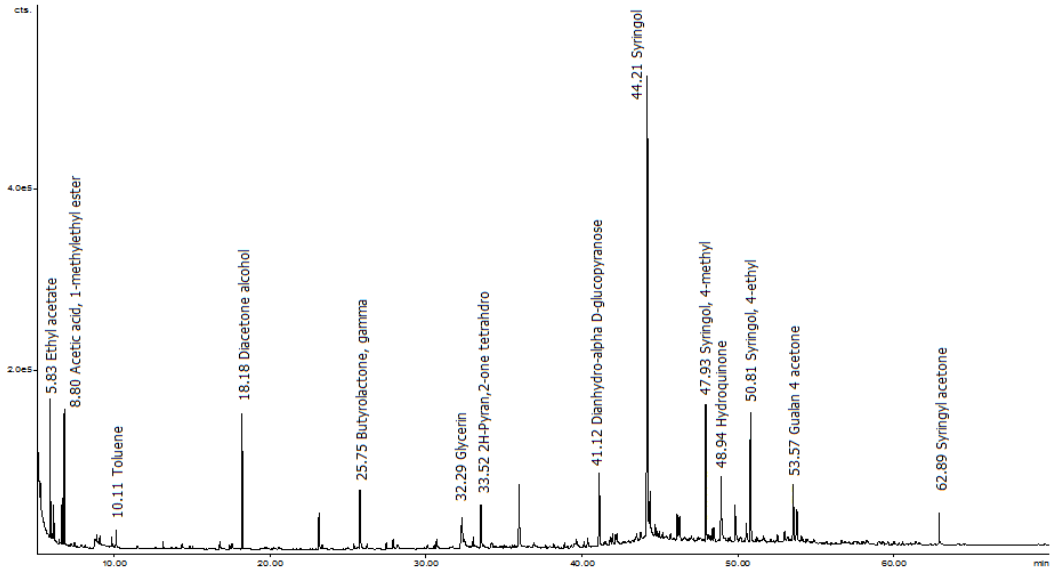

Fig. 3. The chromatograms of leachate obtained from samples treated with 10% solution of bio-oil combined with ELO

Table 5. Fungal Inhibition Test with Four Basidiomycetes Expressed as Mycelium Diameter (mm) After 1 and 2 Weeks of Exposure

Control (mm)	20% bio-oil (mm)	20% bio-oil + ELO (mm)	10% bio-oil (mm)	10% bio-oil + ELO (mm)	Duration
Coniophora puteana					
20	3	0	5	0	1 week
30	5	0	9	0	2 weeks
Gloephyllum trabeum					
20	4	0	10	0	1 week
25	9	0	15	0	2 weeks
Postia placenta					
30	0	0	1	0	1 week
35	0	0	2	0	2 weeks
Trametes versicolor					
90	15	0	0	0	1 week
90	30	0	30	0	2 weeks

All treated samples had significantly lower mass loss than the untreated control samples. The mass loss of the control (untreated) samples was higher than 20% (15% for the white rot fungus), thus confirming the validity of the tests. The decay resistance of the treated wood samples with 20% bio-oil against white and brown rot fungi was very effective (less than 3% weight loss). It is reported that a drawback of bio-oils as wood preservatives is their leachability.

A previous study (Temiz *et al.* 2010) demonstrated that bio-oils are highly leachable from wood, but this can probably be prevented upon proprietary polymerization of its compounds and/or co-impregnation for synergistically enhanced activity. The authors revealed that a significant amount of the phenolic compounds from bio-oils were leached, which was confirmed by UV-Vis results. The additional impregnation with ELO in this study significantly reduced the leachability of bio-oils, particularly when the samples were tested against the fungi *T. versicolor* and *P. placenta*. The efficacy of ELO as a wood protector was previously studied (Terziev and Panov 2011). According to the study, ELO impregnated in Scots pine sapwood at a retention of approximately 100 kg/m^3 is not effective against basidiomycetes and only slightly decreases the wood mass loss compared to the untreated samples. However, the dimensional stability of the treated samples was reported to be significantly improved and thus, a synergic effect was expected when the bio oil in this study was mixed with ELO. A number of authors reported that high retention is required to improve the durability of wood treated with both bio-oils and plant oils (Kartal *et al.* 2010; Temiz *et al.* 2008; Temiz *et al.* 2010; Tomak *et al.* 2011). However, the retention of the studied cane bio-oil was 50 to 100 kg m^{-3}, which is industrially applicable and relatively cheaper than the full cell treatment of plant oils and bio-oils due to low retention. On the other hand, impregnation of wood only with cane oil (20% solution) demonstrated a durability that classifies the treatment as very effective.

The decay resistance of the treated wood samples with bio-oil against brown and white rot fungi can be attributed to the phenolic compounds in the bio-oil. It is reported that phenolic compounds are the main active compounds for antimicrobial activity (Mohan *et al.* 2008; Temiz *et al.* 2010).

Table 6. Weight Loss (%) of the Control and Treated Samples After a Standard Decay Test

Treatment	Oil retention (kg m^{-3})	Weight loss treated, (%)	Weight loss control, (%)
Trametes versicolor			
20% bio-oil + ELO	106.67 (2.61)**	0.99[a]* (0.98)	19.52 (2.60)
20% bio-oil	108.26 (0.61)	1.87[ab] (0.58)	20.25 (1.61)
10% bio-oil + ELO	54.13 (1.97)	1.48[b] (1.15)	15.90 (3.98)
10% bio-oil	52.8 (1.44)	6.88[c] (3.20)	21.13 (3.09)
Postia placenta			
20% bio-oil + ELO	104.53 (3.79)	1.14[a] (0.74)	34.37 (4.88)
20% bio-oil	108.53 (1.82)	1.26[a] (0.39)	41.6 (11.00)
10% bio-oil + ELO	54.13 (1.02)	1.49[a] (1.33)	33.9 (3.63)
10% bio-oil	52.8 (0.43)	5.14[b] (3.16)	32.4 (3.66)
Gloephyllum trabeum			
20% bio-oil + ELO	102.13 (3.93)	1.75[a]* (1.60)	37.35 (7.73)
20% bio-oil	106.41 (2.80)	2.39[ab] (0.35)	28.39 (6.56)
10% bio-oil + ELO	53.06 (1.26)	3.90[b] (1.75)	34.73 (5.31)
10% bio-oil	52.8 (1.30)	3.90[b] (0.44)	27.48 (7.36)
Coniophora puteana			
20% bio-oil + ELO	106.13 (3.31)	0.89[a]* (1.68)	52.12 (2.71)
20 % bio-oil	105.6 (2.80)	2.60[a] (0.55)	54.26 (2.25)
10% bio-oil + ELO	52.4 (1.59)	2.14[a] (0.47)	54.91 (3.75)
10% bio-oil	52.26 (1.15)	2.99[a] (0.48)	57.07 (4.13)

***** Identical letters indicate no statistical significance
** Standard deviation within parentheses

Durability against termites

The results of the termite test with the species *Reticulitermes flavipes* are shown in Table 7.

Table 7. Termite Test Results of Giant Cane Oil

Treatment	Weight loss, (%)	Survival rate, (%)
20% bio-oil	No loss	0
20% bio-oil + ELO	No loss	0
Control	20 (3)*	82 (19)

*Standard deviation in parentheses

According to the test results, no weight losses were observed from treated samples, but control samples showed 20% weight loss. In addition, 82% of the termites survived in the control groups but no termites were recovered from the treated samples. It can be concluded that the bio-oil tested was very effective against *Reticulitermes flavipes*.

Yatagai *et al.* (2002) indicated that wood vinegar was highly effective against *Reticulitermes speratus*, due to the relatively high proportion of acetic and lactic acid in it. It was also reported that shell bio-oil has the potential to be a low-cost and environmentally low-impact wood preservative for preventing attacks by drywood termites (Sunarta *et al.* 2011). However, it was found that wood tar obtained from solid biomass was not effective against subterranean termites (*Coptotermes formosanus*) due to low vanillin content (0.16%) (Kartal *et al.* 2004). As a further step in the investigation of giant cane oil as a wood preservative, comprehensive field tests are planned.

CONCLUSIONS

Water absorption, tangential swelling, fungicidal characteristics, and resistance against *Reticulitermes flavipes* of bio-oil pyrolyzed from giant cane (*Arundo donax*) were evaluated in this study.

1. The chemical composition of the giant cane was 22% lignin and 42% α-cellulose. Bio-oil was obtained by a pyrolysis process at 450 to 525 °C.
2. The identified compounds in the bio-oil were acids, ketones, furans, benzenes, phenols, sugars, guaiacols, and multifunctional compounds.
3. Secondary impregnation with epoxidized linseed oil was performed on the samples previously treated with bio-oil in order to reduce the leachability of the bio-oil. Target retentions were 45 to 100 kg m^{-3}. The hydrophobic characteristic of samples treated with bio-oil was higher than those of the controls (untreated). Epoxidized linseed oil treatment increased the hydrophobicity.
4. Decay resistance of treated wood samples with 20% bio-oil against brown fungi (*Postia placenta, Gloephyllum trabeum, Coniophora puteana*) and white rot fungi (*Trametes versicolor*) was very effective. Phenolic compounds in the bio-oil made up the main group of compounds and played a significant role in the increased decay resistance against brown rot and white rot fungi.
5. Regarding the termite test, 82% of the termites survived in the control groups but no termites were recovered from the samples treated with bio-oil. All bio-oil concentrations tested were effective against *Reticulitermes flavipes.*

ACKNOWLEDGEMENTS

The authors thank Kahramanmaras Sutcu Imam University, Turkey, Hamburg University, and Johann Heinrich von Thünen-Institut (especially Dr. Uwe Noldt for the termite test), Germany. The financial support of the project *Micro- and nano-structural studies on the cell wall distribution and efficacy of modern and novel wood protection systems* by the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS) is gratefully acknowledged.

REFERENCES CITED

ASTM (1992). "D1744: Standard test method for determination of water in liquid petroleum products by Karl Fischer Reagent," ASTM International, West Conshohocken, PA, USA.

Atchison, J. E. (1993). "Data on non-wood plant fibres," *Pulp and Paper Manufacture, Vol. 3: Secondary Fibres and Non-Wood Pulping*, M. J. Kocurek (ed.), TAPPI, 4.

AWPA (2008). "E4: Standard method of testing water repellency of pressure treated wood," American Wood Protection Association Standard.

AWPA (2008). "E11: Standard method of determining the leachability of wood preservatives," American Wood Protection Association Standard.

Azeez, A. M., Meier, D., Odermatt, J., and Willner, T. (2010). "Fast pyrolysis of African and European lignocellulosic biomasses using Py-GC/MS and fluidized bed reactor," *Energy Fuels*.

Demirbas, A. (2004). "Effect of initial moisture content on the yields of oily products from pyrolysis of biomass," *J. Anal. Appl. Pyrolysis* 71, 803-815.

DIN (1997). "51562: Determination of the kinematic viscosity using the standard design Ubbelohde viscometer."

Dobele, G., Urbanovich, I., Volpert, A., Kampars, V., and Samulis, E. (2007). "Fast pyrolysis-effect of wood drying on the yield and properties of bio-oil," *BioResources* 2(4), 699-706.

European Standard (1996). "EN 113: Determination of the toxic values against wood destroying basidiomycetes cultured on agar medium," European Standard.

Ertas, M., and Alma, M. H. (2010). "Pyrolysis of laurel (*Laurus nobilis* L.) extraction residues in a fixed-bed reactor: Characterization of bio-oil and bio-char," *J. Anal. Appl. Pyrolysis* 88, 22-29.

Gallego, E., Roca, F. J., Perales, J. F., Guardino, X., and Berenguer, M. J. (2008). "VOCs and PAHs emissions from creosote-treated wood in a field storage area," *Sci. Total Environ*. 402, 130-138.

Gezer, E. D., Yildiz, U. C., Temiz, A., Yildiz, S., and Dizman, E. (2005). "Cu, Cr and As distribution in soils adjacent to CCA-treated utility poles in eastern Black Sea Region of Turkey," *Build. Environ.* 40(12), 1684-1688.

Gonzalez, J. F., Ramiro, A., Gonzalez-Garcia, C. M., Ganan, J., Encinar, J. M., Sabio, E., and Rubiales, J. (2005). "Catalyzed pyrolysis of grape and olive bagasse. Influence of catalyst type and chemical treatment," *Ind. Eng. Chem. Res.* 44(9), 3003-3012.

Jeon, Y. J., Xun, Z., and Rogers, P. L. (2010). "Comparative evaluations of cellulosic raw materials for second generation bioethanol production," *Lett. Appl. Microbiol.* 51(5), 518-524.

Kartal, S. N., Imamura. Y., Tsuchiya, F., and Ohsato, K. (2004). "Preliminary evaluation of fungidical and termicidal activities of filtrates from biomass slurry fuel production," *Bioresource Technol.* 95, 41-47.

Kartal, S. N., Terzi, E., Kose, C., Hofmeyr, J., and Imamura, Y. (2010). "Biological performance of wood treated with tar-oil recovered during slow pyrolysis of macadamia nut shells," *IRG/WP 10-30524*, The International Research Group on Wood Preservation, France.

Qiang, L., Yang, X.-L., and Zhu, X.-F. (2008). "Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk," *J. Anal. Appl. Pyrolysis* 82(2), 191-198.

Mansoor, H., and Ali, R. M. (1992). "Antifungal activity of pyrolytic oils of tar from rubberwood (*Hevea brasiliensis*) pyrolysis," *J. Trop. Forest Sci.* 4, 294-302.

Mazela, B. (2007). "Fungicidal value of wood tar from pyrolysis of treated wood," *Waste Manage.* 27, 461-465.

Meier, D., Andersons, B., Irbe, I., Chirkova, J., and Faix, O. (2001). "Chapter 128. Preliminary study on fungicide and sorption effects of fast study on fungicide and sorption effects of fast pyrolysis liquids used as wood liquids used as wood preservative," *Progress in Thermochemical Biomass Conversion*, Blackwell Science Ltd., Oxford, UK.

Meier, D., and Faix, O. (1999). "State of the art of applied fast pyrolysis of lignocellulosic materials - A review," *Bioresource Technol.* 68, 71-77.

Mohan, D., Pittman, C. U., and Steele, P. H. (2006). "Pyrolysis of wood/biomass for bio-oil: A critical review," *Energy Fuels* 20, 848-889.

Mohan, D., Shi, J., Nicholas, D. D., Pittman Jr., C. U., Steele, P. H., and Cooper, J. E. (2008). "Fungicidal values of bio-oils and their lignin-rich fractions obtained from wood/bark fast pyrolysis," *Chemosphere* 71(3), 456-465.

Mourant, D., Yang, D.-Q., Lu, X., and Roy, C. (2005). "Anti-fungal properties of the pyroligneous liquor from the pyrolysis of softwood bark," *Wood Fiber Sci.* 73, 542-548.

Mourant, D., Yang, D.-Q., and Roy, C. (2007). "Decay resistance of pyrolytic oil resin-treated wood," *Forest Prod. J.* 57, 30-35.

Panov, D., Terziev, N., and Daniel, G. (2010). "Using plant oils as hydrophobic substances for wood protection," *IRG/WP 10-30550*, 41st IRG on Wood Protection, May 9-13, Biarritz, France.

Rydholm, S. A. (1976). *Pulping Processes*, Interscience Publishers, New York, Chichester, Brisbane, Toronto.

Shatalov, A. A., Quilho, T., and Pereira, H. (2001). "*Arundo donax* L. reed: New perspectives for pulping and bleaching 1. Raw material characterisation," *Tappi Journal Peer Reviewed Paper* 84(1).

Sunarta, S., Darmadji, P., Uehara, T., and Katoh, S. (2011). "Production and characterization of palm fruit shell bio-oil for wood preservation," *Forest Prod. J.* 61(2), 180-184.

TAPPI (1992). *TAPPI Test Methods 1992-1993*, Tappi Press Atlanta, Georgia, USA.

Temiz, A., Alma, M. H., Terziev, N., Palanti, S., and Feci, E. (2010). "Efficiency of bio-oil against wood destroying organisms," *J. Biobased Mater. Bioenergy* 4, 1-7.

Temiz, A., Panov, D., Terziev, N., and Hafren, J. (2008). "Research on silicones and oils as hidrophobic agents," *V. Congreso Nacional De protection De La Madera*, San Sebastian, Spain.

Temiz, A., Terziev, N., Eikenes, M., and Hafren, J. (2007). "Effect of accelerated weathering on surface chemistry of modified wood," *Applied Surf. Sci.* 253, 5355-5362.

Terziev, N., and Panov, D. (2011). "Plant oils as "green" substances for wood protection," In: *Minimising the Environmental Impact of the Forest Products Industries*, F. Caldeira, and F. Pessoa (eds.), Porto, Portugal, ISBN 978-989-643-083-2, pp. 143-149

Tomak, E. D., Viitanen, H., Yildiz, U. C., and Hughes, M. (2011). "The combined effects of boron and oil heat treatment on the properties of beech and scots pine wood. Part 2: Water absorption, compression strength, color changes, and decay resistance," *J. Material Sci.* 46, 608-615.

Ucar, G., and Balaban, M. (2003). "Hydrolysis of polysaccharides with 77% sulfuric acid for quantitative saccharification," *Turk. J. Agric. For.* 27, 361-365.

Yatagai, M., Nishimoto, M., Hori, K., Ohira, T., and Shibata, A. (2002). "Termiticidal activity of wood vinegar, its components and their homologues," *J. Wood Sci.* 48(4), 338-342.

Article submitted: November 5, 2012; Peer review completed: February 16, 2013;
Revised version received and accepted: February 27, 2013; Published: March 1, 2013.