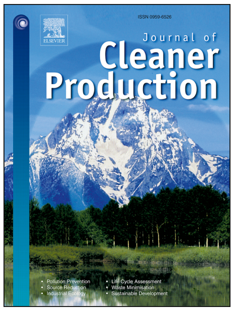

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Optimization of thermal desorption conditions for recovering wood preservative from used railroad ties through response surface methodology

Pyoungchung Kim[1*], Holly L. Haber[2, 3], Jeff Lloyd[4], Jae-Woo Kim[4], Nourredine Abdoulmoumine[3] and Nicole Labbé[2*]

[1] TerraPower LLC., 330 120th Avenue NE, Suite 100, Bellevue, WA 98005, USA

[2] Center for Renewable Carbon, the University of Tennessee, 2506 Jacob Dr., Knoxville, TN 37996, USA

[3] Biosystems Engineering & Soil Science, the University of Tennessee, 2506 E.J. Chapman Dr. Knoxville, TN 37996, USA

[4] Nisus Corp., 100 Nisus Dr. Rockford, TN 37853, USA

*Corresponding authors.

Pyoungchung Kim:pyoungchung@gmail.com (865) 924-5892. Fax: (865) 946-1109

Nicole Labbé: nlabbe@utk.edu, Phone: (865) 946–1126. Fax: (865) 946–1109

Abstracts

A statistical response surface methodology (RSM) using a central composite design (CCD) model was applied to identify the optimum thermal desorption conditions for maximum recovery of preservative from copper naphthenate (CuNap) treated wood and subsequent production of a high quality pyrolytic vapor from the thermally treated wood. From the designed experiment, 94 % of the total preservative present in the ties was desorbed at temperatures higher than 250 ºC and residence times longer than 30 min. Elevating the temperature from 215 ºC to 285 °C for 45 min residence time generated a weight loss of 12 to 36 wt%, an increase in higher heating value (HHV) from 20.1 to 21.9 MJ/kg, and a reduction of energy yield from 90.4 to 71.5 % of the resulting thermally treated biomass. Pyrolysis at 450 °C of this material produced a vapor rich in sugars- and lignin-derived compounds. The predicted optimum conditions in terms of a maximum preservative recovery, minimum energy yield loss of the wood, and production of thermally treated biomass that generates a high proportion of sugars- and lignin-derived compounds during pyrolysis were found to be 265 ºC and 51 min. Under these optimum conditions, the predicted maximum preservative recovery was 95 % while the predicted thermally treated solid retained 77 % of the original energy yield and produced high portions of levoglucosan and lignin-derived compounds during subsequent pyrolysis, similar to torrefied wood.

Key words: Bio-oil, naphthenic acids, pyrolysis, response surface methodology, used railroad ties

1. Introduction

Wood products are treated with preservative to provide long-term protection against fungal decay and termite attack in a wide variety of residential, commercial, agricultural, and industrial construction applications such as decking, buildings, bridges, utility poles, and railroad ties. The service life of these preserved wood products varies depending on the types of preservative, exposure environment, applied loadings, product quality, and maintenance (Bolin and Smith, November 2010). The United States Environmental Protection Agency (U.S. EPA) has registered water- and oil-borne preservatives for various applications; water-borne solutions like micronized copper azole are used for residential building applications. While oil-borne preservative, for restricted (creosote and pentachlorophenol) and non-restricted (copper naphthenate) use, are mostly utilized for industrial applications. The estimated annual production of preserved wood in the U.S. is reported to be approximately 18,000,000 m^3 including 2,400,000 m^3 of creosote treated wood for primarily rail ties, 900,000 m^3 of oil-borne (primarily pentachlorophenol) preservative treated wood for utility poles, and 14,700,000 m^3 of water-borne preserved wood products (Vlosky, 2009). Copper naphthenate (CuNap)-treated wood is being increasingly preferred for both poles and ties and is the focus of this work. Copper naphthenate consists of copper and naphthenic acid typically diluted in oil (No. 2 fuel oil). Naphthenic acid is a natural component of crude oil and is a complex mixture of organic acids (single or fused aliphatic rings, naphthenic, alkylated in various positions with aliphatic groups and monocarboxylic acid) (Holowenko et al., 2002). The market acceptance of CuNap is growing as it is perceived as being equal to or better in performance to creosote or pentachlorophenol for both ties and poles (Barnes et al., 2001). Additionally, copper naphthenate has a similar cost and much lower environmental, health and safety impacts than the other oil-borne preservative.

Utilization of preserved wood after its primary service life has included reuse in track, an energy source for co-generation to produce combined heat and power, commercial and residential timbers, or disposal in landfills (Smith, 2015). However, the current low cost of natural gas and new regulations under the non-hazardous secondary material (NHSM) rule of the U.S. EPA has increased the number of ties and poles going to landfill. Landfilling is not an environmentally friendly solution since the released preservative contaminates soil and ground water and the wood degrades to greenhouse gases such as carbon dioxide and methane (Bolin and Smith, November 2010). A proposed rule under NHSM recognizes CuNap treated wood with regard to hazardous air pollutants and allows its adoption as carbon neutral boiler fuel. However, there may be more efficient uses of this material, if the value of the preservative can be captured for re-use, and the material quality further improved for either boiler fuel or pyrolysis. Any improvement in the competitiveness of this fuel versus CO_2 producing natural gas would also be highly beneficial.

In addition to boiler fuel and gasification, a few research groups have investigated fast pyrolysis to convert used preservative-treated wood into bio-oil containing preservative, biochar, and non-condensable gases (Jung et al., 2013; Mazela, 2007). In the previous studies (Haber et al., 2017; Kim et al., 2016a; Kim et al., 2016b; Kim et al., 2017), a thermal desorption process was applied to efficiently recover wood preservative with minimum degradation of the wood matrix from creosote-treated ties at 250 – 350 ºC in the absence of oxygen. It was demonstrated that up to 79 % of the total creosote present in the ties could be desorbed and recovered while improving the biomass quality by increasing its carbon content, caloric value, and significantly reducing the creosote residues in the thermally treated wood. These studies evidenced that thermal desorption of preservative-treated wood has the advantages of lower costs and higher preservative recovery rates, producing a high quality biomass for further thermochemical conversion, compared to solvent extraction (Levien et al. 1994) and biological detoxification processes (Lamar et al. 1992). The objective of this study is to investigate the optimal desorption conditions for CuNap-treated wood using a statistical approach, i.e. response surface methodology (RSM). This approach has the advantage of minimizing the number of experimental runs, thus saving time, while identifying the effect of the main factors (temperature and reaction time) and their interactions. The experiment was designed to determine the optimal conditions of these main factors during the desorption process by considering responses such as preservative recovery yield, weight loss, energy yield of thermally treated wood ties, and yield and quality of pyrolytic vapor of the thermally treated wood.

2. Material and methods

2.1. Material

Used copper naphthenate (CuNap)-treated railroad ties were obtained from Nisus Corp. (Rockford, TN, USA). The ties were chipped and then ground into less than 2 mm particle sizes with a knife mill before testing.

2.2. Experimental design

2.2.1. Thermal desorption

The thermal desorption experiments were carried out in a bench-scale fixed-bed batch reactor equipped with a condensation system (Supporting information Fig A1). In brief, a vertical furnace was outfitted with a cylindrical quartz tube (internal diameter 47 mm and length 610 mm), which was connected to a series of four liquid nitrogen-cooled Dewar-type glass condensers. For each run, 30 g of wood tie sample were loaded into a basket holder made of stainless steel with mesh (pore size 0.37 mm, diameter 32 mm, length 250 mm) and inserted into the bottom of the quartz tube, away from the heated zone. The furnace was then heated to the desired temperature at a heating rate of 10 ºC/min with a constant flow rate (4L/min) of nitrogen purge gas. After the desired temperature was reached and isothermalized, the sample holder was raised up into the heated zone of the quartz tube in the furnace, where the wood sample was thermally treated for a specific residence time. At the completion of the experiment, the sample holder was lowered to the bottom of the quartz tube and cooled under continuous nitrogen flow. The vapors produced during the thermal desorption were swept by the purge gas from the reactor into the condensers. Each run was conducted in duplicate. The thermally treated materials in the holder were weighed and characterized after each desorption.

2.2.2 Response surface design

Response surface methodology (RSM) using a central composite design (CCD) (Bezerra et al., 2008; Box and Wilson, 1951) was employed to minimize the number of experiments for optimizing the thermal desorption conditions of wood preservatives present in the railroad wood tie samples. The design of experiment consisted of 2^2 factorial design with two main factors (temperature and reaction time) with five levels of temperature (215, 225, 250, 275, and 285 ºC) and reaction time (20, 30, 45, 60, and 70 min). A total of 13 runs of the thermal desorption were conducted, including five center runs (250 °C, 45 min), two factors with two levels (225 and 275 °C, 30 and 60 min), and four axial runs (α = 215 and 285 °C, 20 and 70 min) with the design rotatable (Table 1). These factors were coded as independent variables, x_1 for temperature and x_2 for reaction time in the statistical model. The response surface analysis was conducted using JMP software version 12 (SAS Institute Inc.) and a second order polynomial regression model was selected to approximate the response. Additionally, an analysis of variance (ANOVA) was performed to evaluate the fitness of the quadratic regression models with a 95 % confidence level. A statistical F-test (F-value) was used to determine the significance of effects.

Run	Central composite design	Independent variable			
		Coded variable		Variable	
		Temp. (x_1)	Time (x_2)	Temp (°C)	Time (min)
1	Axial point	-1.4	0	215	45
2	Factorial point	-1	-1	225	30
3		-1	1	225	60
4	Axial point	0	-1.4	250	20
5	Central point	0	0	250	45
6		0	0	250	45
7		0	0	250	45
8		0	0	250	45
9		0	0	250	45
10	Axial point	0	-1.4	250	70
11	Factorial point	1	-1	275	30
12		1	1	275	60
13	Axial point	1.4	0	285	45

Table 1. Experimental matrix for central composite design for two independent variables.

2.3. Characterization

The untreated and thermally treated wood samples were characterized by the following analytical techniques. Moisture content was measured by the Karl-Fischer titration method (Kim et al., 2016a). Volatile matter, ash content, and fixed carbon were measured by proximate analysis according to American Society for Testing and Materials (ASTM D1762-8). The higher heating value (HHV, MJ/kg) was calculated based on the proximate analysis results using the equation 1 (Cordero et al., 2001). Energy yield (%), defined as the amount of HHV retained in the solid after thermal desorption, was calculated from the weight loss and HHV values in the untreated and thermally treated wood samples by equations 2 and 3 as follows (Bergman et al., 2004).

$$HHV\left(\frac{MJ}{kg}\right) = 0.3543 \times fixed\ carbon\ (\%) + 0.1708 \times volatile\ matter\ (\%) \qquad \text{(eq. 1)}$$

$$M_p(\%) = \frac{M_t}{M_o} \times 100 \qquad \text{(eq. 2)}$$

$$Energy\ yield\ (\%) = (M_p \times H_t)\frac{(M_p \times H_t)}{H_o} \times 100 \qquad \text{(eq. 3)}$$

where M_p is weight yield (wt%); M_t is weight of thermally treated wood; M_o is weight of untreated sample; H_t is HHV of thermally treated sample; H_o is HHV of untreated sample.

Surface functionality of the solid and liquid fractions generated by the thermal treatment was investigated by Fourier transform infrared (FTIR) spectroscopy in an attenuated total reflectance mode (PerkinElmer Spectrum One spectrometer, FTIR-ATR). A small sample was deposited on a diamond ATR crystal and a spectrum (4000 – 600 cm^{-1}) was acquired. A total of six spectra per sample were collected at a 4 cm^{-1} resolution and displaced in absorbance values. Removal efficiency of preservative from the tie samples was calculated using the IR peak areas between 3000 and 2800 cm^{-1}.

Pyrolytic vapor of the different thermally treated samples was investigated by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS, Perkin Elmer Clarus 680 Gas Chromatography/Clarus SQ 8C Mass Spectrometer with a Frontier EGA/Py-3030 D micropyrolyzer). Sample pans were layered with 0.4 mg of material and dropped via the auto sampler into the pyrolysis furnace and pyrolyzed at 450 ºC for 12s. The vapor produced by pyrolysis was swept into a GC-injection port (temperature 270 °C) by a GC carrier gas (helium, 1mL/min). The vapor was then separated using an DB-1701 capillary column (60 m length x 0.25 mm ID x 0.25 μm film thickness, Agilent), and analysed using a mass spectrometer (source temperature 270 °C, 70 eV electron ionization). Three pyrograms per sample were collected. A total of 300 chromatographic peaks were extracted from each pyrogram using a peak height to noise ratio of ≥ 10 and compared to the National Institute of Standards and Technology (NIST) library of fragmentation patterns for identification. The peaks in the chromatogram were normalized to peak area percentages calculated from the quotient of individual peak area and total peak area.

2.4. Multivariate statistical analysis

The collected FTIR spectra were analysed using the multivariate statistical method, principal component analysis (PCA), to classify the samples by their spectral features (Unscrambler software version 9.0, CAMO, Woodbridge, NJ). PCA is a variable reduction process that orthogonally transforms complex and large dataset into a new data set, called principal components (PCs), that retains most of the information regarding the original variables (Labbé et al. 2006). Each PC explains the variance in the data through scores and loadings plots. The scores plot describes the relation between samples and visualize any clustering or pattern in the dataset in the new axis of principal components. The loadings plot estimates the relationship between the variables (i.e. wavenumbers) and determines which spectral region contributes the most to the separation and/or classification of the samples.

3. Results and discussion

3.1. Weight loss by thermal desorption

The weight loss of thermally treated wood tie samples increased with both, temperature and reaction time (Table 2). An elevation in temperature had a substantial effect on the weight loss of the material. For example, the sample treated at 215 ºC for 45 min showed a 12.0 wt% weight loss, but when the temperature was raised to 250 and 285 ºC for 45 min, weight loss significantly increased to 21.8 and 36.1 wt%, respectively. Reaction time also impacted weight loss; reaction time from 30 to 60 min at 225 ºC increased weight loss from 10.5 to 14.4 wt% whereas reaction time from 20 to 70 min at 250 ºC led to an increase in weight loss from 11.6 to 24.9 wt%. Furthermore, reaction time from 30 to 60 min at 275 ºC resulted in a high weight loss from 27.5 to 33.7 wt%. The experimental data of weight loss (Table 2) were fitted to a full quadratic second-order polynomial equation (the results are described in the Supporting information Table A1 and Fig. A2). The results demonstrated that the linear terms (temperature and time) and quadratic terms (temp^2 and time^2) had a significant effect on weight loss during thermal desorption (Table 3). Among the model terms, temperature exhibited the most significant effect on weight loss.

Variable	Weight	Proximate analysis (dry basis, %)	HHV[5)]	Energy

Temp (°C)	Time (min)		Water[1] content	Volatile matter	Fixed [2] carbon	Ash		
Untreated		0.0	7.7[3] (0.3)	84.6 (0.5)	14.3 (0.5)	1.1 (0.0)	19.5 (0.1)	100.0
215	45	12.0 g[4] (0.9)	0.6 (0.0)	81.6 (1.0)	17.3 (1.0)	1.2 (0.0)	20.1 (0.2)	90.4 a[4] (0.8)
225	30	0.5 g (0.3)	2.9 (0.0)	83.2 (0.5)	16.2 (0.4)	0.6 (0.1)	20.0 (0.1)	91.5 a (0.3)
225	60	14.4 f (1.1)	2.5 (0.1)	83.4 (0.3)	16.2 (0.3)	0.4 (0.0)	20.0 (0.1)	87.6 b (0.3)
250	20	1.6 g (0.8)	1.4 (0.1)	81.8 (0.5)	17.1 (0.5)	1.0 (0.0)	20.1 (0.1)	90.8 a (0.4)
250	45	21.8 e (0.6)	1.4 (0.1)	79.2 (0.3)	19.7 (0.3)	1.1 (0.1)	20.5 (0.1)	82.1 c (0.4)
250	70	24.9 d (0.1)	0.7 (0.6)	77.7 (0.6)	21.1 (0.6)	1.1 (0.0)	20.8 (0.1)	79.9 d (0.5)
275	30	27.5 c (0.5)	1.2 (0.3)	77.5 (1.2)	21.3 (1.1)	1.3 (0.2)	20.8 (0.2)	77.1 e (0.6)
275	60	33.7 b (0.4)	1.0 (0.4)	73.9 (0.7)	24.7 (0.9)	1.4 (0.2)	21.4 (0.2)	72.6 f (0.7)
285	45	36.1 a (0.5)	0.5 (0.0)	71.4 (0.3)	27.3 (0.3)	1.4 (0.0)	21.9 (0.1)	71.5 f (0.2)

[1] Water content was measured using a Karl Fischer titration method.

[2] Fixed carbon was calculated by difference (100 % - volatile matter – ash content).

[3] Mean and standard deviation in parenthesis (n=3).

[4] ANOVA analysis, p<0.05, levels not connected by same letter are significantly different.

[5] HHV = $0.3543 \times fixed\ carbon\ (\%) + 0.1708 \times volatile\ matter\ (\%)$

Table 2. Weight loss, proximate analysis, HHV, and energy yield of untreated and thermally treated CuNap-wood materials.

Table. 3. Model equations of response variables.

Response variable		Model equation	R^2 [4]
Weight loss %		$Y=21.8 +8.3x_1+3.6x_2+1.2x_1^2-1.4x_2^2$	0.97
Preservative removal by FTIR[2]		$Y=4.1-0.7x_1 - 0.8x_2+0.6x_1x_2+0.1x_1^2+0.4x_2^2$	0.93
Energy yield %		$Y=82.2-7.0x_1 -2.9x_2-0.1x_1x_2-0.9x_1^2+1.3x_2^2$	0.97
Pyrolytic compounds %	Preservative removal %	$Y=93.9+6.5x_1+9.5x_2-6.3x_1x_2-2.7x_1^2-7.8x_2^2$	0.93
	Total pyrolytic peak area%	$Y=79.5-6.9x_1 -3.7x_2+3.4x_1x_2-1.1x_1^2+2.6x_2^2$	0.99

at 450 °C by Py-GC/MS[3)]	Light oxygenates	$Y= 32.0 - 2.2x_1 - 1.1x_1^2$	*0.87*
	Furans/pyrans	$Y=5.8 - 0.5x_1+0.1x_2 - 0.2x_1{\ast}x_2$	*0.92*
	Levoglucosan	$Y=17.6 + 2.8x_1+1.3x_2$	*0.95*
	Lignin	$Y=42.9 +1.6x_1+ 1.0x_2 -1.4x_2^2$	*0.93*

[1)] x_1 and x_2 represent independent coded variables of temperature and time, respectively.
[2)] Preservative was determined by FTIR using peak area between 3000 and 2800 cm^{-1}.
[3)] Pyrolytic compounds were determined by chromatographic peak area % produced from thermally treated wood ties using Py-GC/MS at 450 °C.
[4)] R^2 represents coefficient of determination (adjusted R^2).

3.2. Preservative determination in the CuNap-treated ties by FTIR

Since it was difficult and not practical to completely recover all the preservative from the liquid nitrogen-cooled condensers and only a small amount was collected, it was not possible to accurately quantify the amount of recovered preservative. Instead, the removal efficiency of preservative using a FTIR method (Fig. 1) was determined. The FTIR spectrum of the recovered preservative (Fig. 1a) from the condensers was very similar to that of commercially available pure naphthenic acid, showing major bands at 2972 - 2922 cm^{-1} and 1463 cm^{-1} which are assigned to C-H stretching and C-H bending, respectively, for alkyl groups in naphthenic acid and diluent oil (Table 4) (Craciun and Kamdem, 1997). The band at 1708 cm^{-1} was assigned to the carbonyl group (C=O) present in the carboxylic acid of naphthenic acid. The intensity of the band at 2922 cm^{-1} was higher than the band at 1708 cm^{-1} in the recovered preservative indicating the presence of high diluent oil and low naphthenic acid content in the recovered preservative (these two bands had similar intensity in the pure naphthenic acid) (Fig. 1a). The spectrum of the commercial copper-naphthenate solution with 0.8 % naphthenic acid in diluent oil (typically No. 2 fuel oil) showed a peak at 1590 cm^{-1} which was assigned to C=O stretching in Cu-acetate and was not observed in the spectra of recovered preservative and pure naphthenic acid. These findings demonstrated that during thermal desorption, the organic preservative components, including naphthenic acid and diluent oil were desorbed.

Wavenumber (cm^{-1})	Assignment
3483, 3349, 3265	O-H stretching
2922, 2870	Aliphatic C-H stretching
1724	C=O stretching in COOH
168	
161	
151	
146	

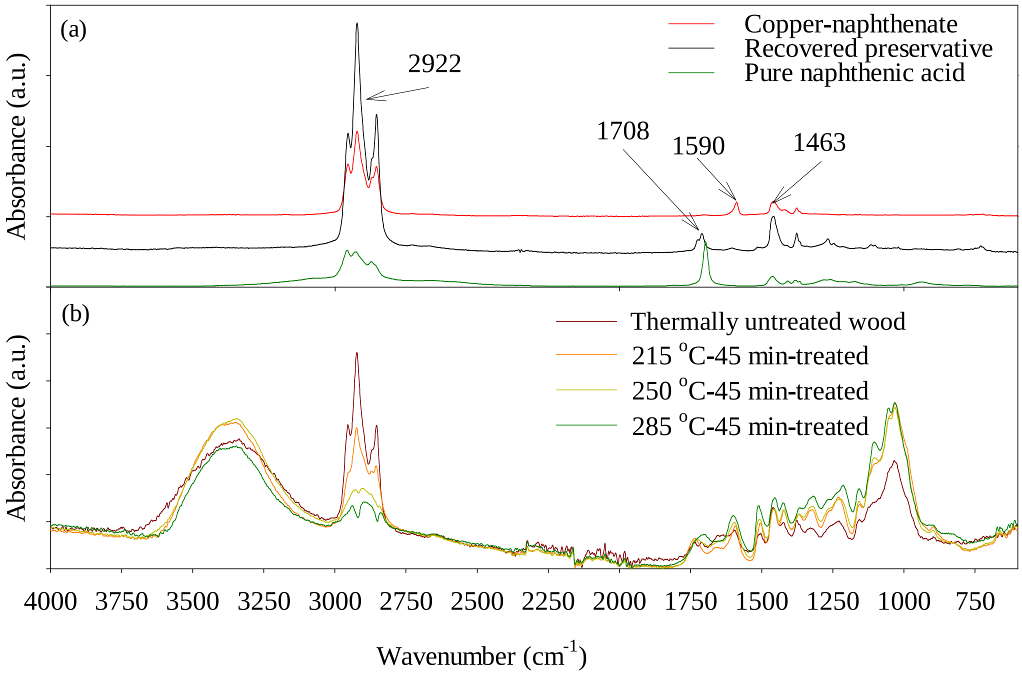


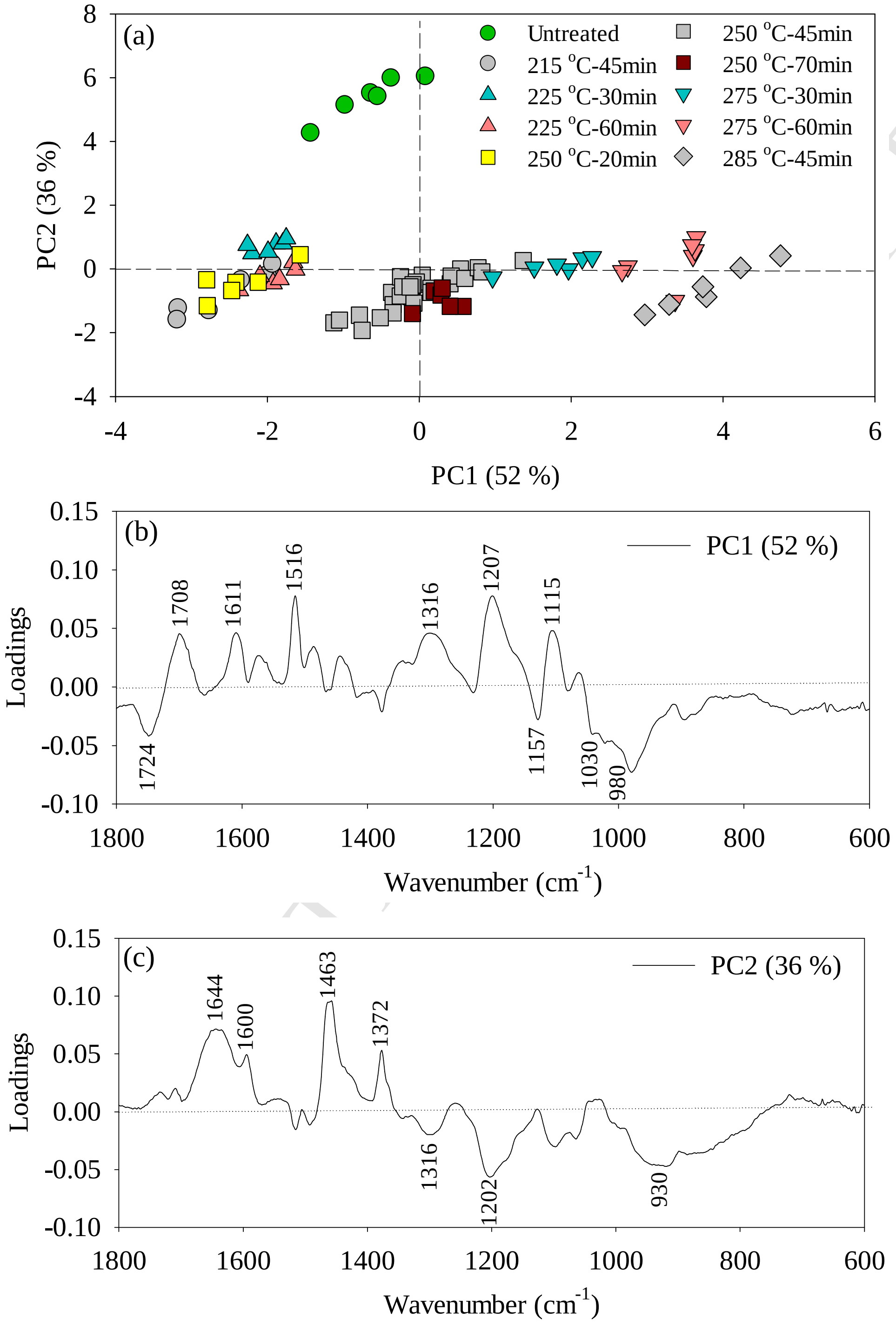
Fig. 1. FTIR spectra of naphthenic acid, recovered preservative components, CuNap treated and its thermally treated wood samples. (a) Recovered preservative, copper naphthenate, and pure naphthenic acid and (b) untreated and thermally treated CuNap wood samples.

Table 4. FTIR wavenumbers and assignments of CuNap-treated and thermally CuNap-treated wood samples (Bernini et al., 2016; Fatriasari et al., 2017).

1422	Aromatic ring stretching with in plane C-H deformation
1372	C-H deformation
1326	C-O stretching
1316	C-H vibration
1267	C-O stretching
1235	C=O stretching
1207	(C-H) ring
1157	C-O-C vibration
1115	Aromatic C-H deformation
1030	C-O stretching of primary alcohol, C-H bending in plane
980	C-O valence vibration
930	Glycosidic linkage

To delineate the differences in the FTIR spectra between the thermally CuNap treated samples and the starting materials (Fig. 1b), principal component analysis (PCA) was performed separately on two spectral regions; 1800 – 600 cm^{-1} and 4000 – 2600 cm^{-1} (Fig. 2). For the 1800 – 600 cm^{-1} spectral data, the scores plot of the PCA (Fig. 2a) displayed that the thermally treated wood samples with increasing temperature and time shifted from the negative to the positive quadrant of the first principal component (PC1, 52 % of the total spectral variance). The corresponding loadings plot (Fig. 2b) showed that samples treated at higher temperatures and longer times had a higher intensity of lignin bands ranging between 1611 and 1511 cm^{-1} and lower intensity of bands associated with carbonyl groups C=O at 1724, 1030, and 980 cm^{-1}; all indicating the degradation of hemicellulose and cellulose in the wood matrix. The untreated

CuNap tie sample also apparently separated from the thermally treated samples by the second principal component (PC2, 36 % of total spectral variance). The corresponding loadings plot (Fig. 2c) confirmed that –C=O in the carboxyl group (1724, 1644, and 1600 cm^{-1}) and C-H bend (1463 and 1372 cm^{-1}) present in naphthenic acid were removed during the desorption process. PCA of the region between 4000 and 2600 cm^{-1} (Fig. 2d and 2e) demonstrated that the intensity of C-H stretch at 2922 and 2870 cm^{-1} for alkyl groups present in the CuNap treated samples was significantly reduced with increasing desorption temperature and time (PC1, 93 % of total spectral variance).


(a)
Untreated
215 °C-45min
225 °C-30min
225 °C-60min
250 °C-20min
250 °C-45min
250 °C-70min
275 °C-30min
275 °C-60min
285 °C-45min
PC2 (36 %)
PC1 (52 %)
8
6
4
2
0
-2
-4
-4
-2
0
2
4
6
(b)
PC1 (52 %)
Loadings
0.15
0.10
0.05
0.00
-0.05
-0.10
1708
1611
1516
1316
1207
1115
1724
1157
1030
980
1800
1600
1400
1200
1000
800
600
Wavenumber (cm-1)
(c)
PC2 (36 %)
Loadings
0.15
0.10
0.05
0.00
-0.05
-0.10
1644
1600
1463
1372
1316
1202
930
1800
1600
1400
1200
1000
800
600
Wavenumber (cm-1)

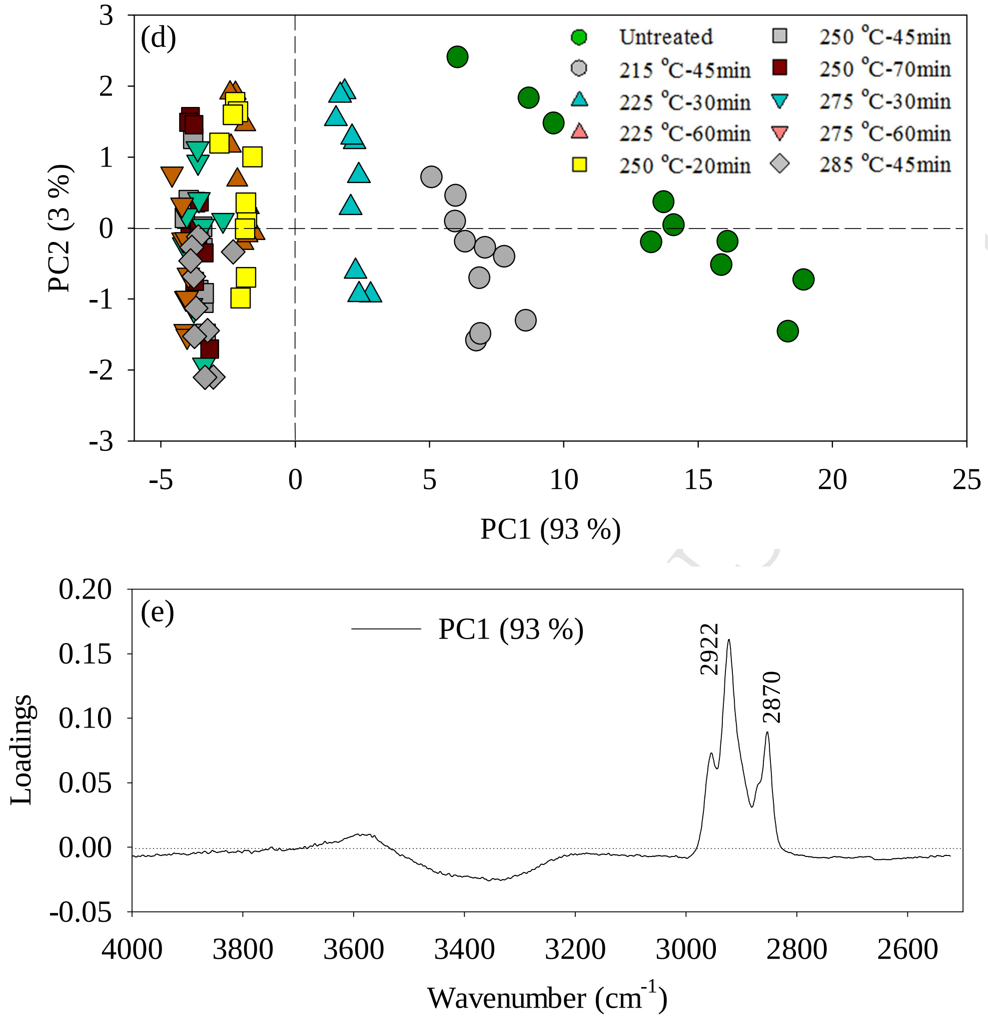


Fig 2. PCA of the FTIR spectra of Cu-Nap treated and thermally Cu-Nap treated ties. (a) Scores and loadings plots (b and c) of PCA for the 1800 - 600 cm^{-1} region and (d) scores and loadings plots (e) of PCA for the 4000 - 2600 cm^{-1} region.

Since the intensity of the bands associated to –C=O in carboxyl groups at 1724 and 1611 cm^{-1} and C-H in alkyl groups at 1463 and 1372 cm^{-1} of naphthenic acid was too low and overlapped with functional groups of the wood matrix, the peak area between 3000 and 2800 cm^{-1} (C-H stretching) for preservative quantification was used. Thermal treatment of the tie samples significantly desorbed preservative reflected by a significant reduction of the IR peak areas between 3000 and 2800 cm^{-1} (Table 5). Interestingly, the peak areas of the samples treated at 225 °C for 60 min and at temperature higher than 250 °C and reaction time lower than 45 min were not significantly different (Table 5), which indicated that most of the organic preservative components were removed from the ties. The peak area values were fitted into the quadratic model (Supporting information Table A2 and Fig. A3) and demonstrated that linear terms (temperature or time), interaction term (temp. x time), and quadratic term (time^2) had a significant impact on C-H groups (i.e. desorption of organic constituents of the preservative) during the thermal treatment (Table 3). Reaction time had a higher impact on the desorption of preservative than temperature and the combination of both parameters.

Table 5. FTIR peak areas at 2922 cm^{-1} and chromatographic peak areas by Py-GC/MS at 450 ºC for preservative determination in the untreated and thermally treated CuNap ties.

Independent variable		Response variable		
		FTIR$^{1)}$ peak area at 2922 cm^{-1}	Chromatographic peak area by Py-GC/MS at 450 ºC	
Temp (°C)	Time (min)		Total peak area (%)	Removal % of preservatives
Untreated		9.8 (0.5)$^{1)}$	100.0	0.0
215	45	4.7 (0.7) c$^{2)}$	87.4 (3.5) ab	78.5 (2.1) c
225	30	7.0 (0.7) a	94.8 (4.0) a	67.1 (0.2) b
225	60	4.1 (0.4) d	81.0 (1.8) bc	93.1 (1.5) d
250	20	5.9 (0.6) b	90.3 (2.0) b	60.3 (1.9) a
250	45	4.2 (0.3) d	80.0 (0.9) bc	94.8 (0.4) d
250	70	4.0 (0.2) d	79.1 (0.3) bc	94.4 (0.3) d
275	30	4.2 (0.3) d	74.7 (3.2) cd	93.7 (0.6) d
275	60	4.2 (0.1) d	74.4 (2.5) cd	94.3 (0.7) d
285	45	4.0 (0.5) d	67.1 (2.2) d	96.3 (0.6) d

1) FTIR peak area at 2922 cm^{-1} represents peak area calculated between 3000 and 2800 cm^{-1}

2) Mean and standard deviation in parenthesis (n=3).

3) ANOVA analysis $p<0.05$, levels not connected by same letter are significantly different.

3.3. HHV and energy yield of thermally treated wood ties

Proximate analysis of the CuNap-treated wood and the resulting thermally treated solid samples also exhibited a considerable reduction of volatile matter, which was due to the desorption of preservative and partial degradation of the wood matrix with increasing temperature and reaction time (Table 2). At a temperature higher than 275 ºC and 60 min, the amount of volatile matter was reduced from 84.6 wt % to less than 73.9 wt %. Reaction time also had an apparent impact on the reduction of volatile matter at temperatures above 250 ºC. The higher heating value (HHV) calculated based on the proximate analysis data indicated that a decreased volatile matter content and an increased fixed carbon content improved the HHV from 19.5 MJ/kg for the starting material to 21.9 MJ/kg for the 285 ºC and 45 min-treated sample. Energy yield (HHV retained, %) calculated from the weight loss and HHV values showed that as desorption severity augmented, energy yield gradually decreased to 71.5 % at 285 ºC for 45 min (Table 2). The energy yield (%) of the thermally treated samples was fitted to a quadratic model (Supporting information Table A3 and Fig. A4) and demonstrated that both the linear (temperature and time) and quadratic term (time^2) significantly impacted the energy yield during thermal desorption (Table 3). Among the model terms, temperature had a stronger impact than reaction time on the energy yield. Energy yield is another important response variable to optimize thermal desorption conditions when considering the upgradability of thermally treated wood materials for thermochemical processes such as pyrolysis, combustion, or gasification.

3.4. Pyrolytic products at 450 ºC of thermally treated wood ties

The yield and composition of the pyrolytic vapor of thermally treated samples at 450 °C were investigated by Py-GC/MS to assess the quality of the thermally treated biomass as a potential feedstock for bio-oil production via fast pyrolysis (Fig. 3). The identified pyrolytic compounds were categorized as light oxygenates, furanic/pyranic compounds, levoglucosan, phenolic compounds, and preservative compounds (Fig. 4b and Table 6). Pyrolysis of the samples thermally treated under elevated temperatures and reaction times generated a gradual reduction of the total chromatographic peak area (%) compared to that of the untreated CuNap sample (Table 5 and Fig. 4a). The peak area % of the preservative components (naphthenic acid and diluent oil) remaining in the biomass after thermal treatment gradually diminished with increasing desorption severity (Table 4 and Fig. 4b). Peak area % of the pyrolytic products resulting from the pyrolysis of the wood matrix decreased with developing treatment severity (Table 4 and Fig. 4b), indicating that during thermal desorption, the wood matrix was decomposed into smaller oxygenated compounds. In general, wood components thermally decompose under various temperature ranges (Mohan et al., 2006). For example, the degradation of hemicellulose takes place between 220 and 315 ºC with maximum decomposition at 270 - 280 ºC whereas cellulose degradation is not significant within this temperature range and is reported to start at 270 ºC and accelerates at temperatures above 300 ºC. Lignin decomposition begins at a temperature as low as 200 ºC with relatively slower kinetics than hemicellulose and takes place over a wide temperature range (up to 500 ºC). Therefore, a thermal desorption process with higher severity produces treated wood with a lower proportion (%) of hemicellulose and relatively higher cellulose and lignin content than that of untreated wood. The findings also demonstrated that pyrolytic products at 450 °C of wood treated at a higher severity possessed a different distribution (%) of products with a relatively lower proportion (%) of light oxygenates derived from hemicellulose and higher proportion of levoglucosan from cellulose and phenolic compounds from lignin (Fig. 4b). When thermally treated materials were pyrolyzed at 450 ºC using Py-GC/MS, the yield of light oxygenated compounds gradually reduced with raising thermal desorption severity. Furanic/pyranic compounds also gradually diminished with higher severity. The decrease in yield of light oxygenates and furanic/pyranic compounds with desorption severity was due to the reduction of hemicellulose during the thermal treatment, decomposing into water, CO_2, acetic acid, formaldehyde, furfural and formic acid (Dalluge et al., 2014). The yield of levoglucosan and phenolic compounds gradually rose with severity. A significant lower hemicellulose content in the thermally treated wood with increasing desorption severity augmented the proportion (%) of cellulose and lignin in the wood. The previous study (Holly et al., 2017) verified the thermal degradation of wood structures using scanning electron microscopy (SEM). The SEM images showed intervessel pitting and scalariform perforations, typical of hardwoods, for the thermally treated wood samples at 250 and 275℃, which morphologically decomposed almost completely at 300℃ due to degradation of cellulose, hemicellulose, and lignin (Mohan et al., 2006).

The total chromatographic peak area (%) of thermally treated samples produced by Py-GC/MS was fitted to a second-degree polynomial model as the response surface methodology. The ANOVA results confirmed that temperature had a higher impact than reaction time and other model terms (Table 3, Supporting information Table A4 and Fig. A5). The fitting of removal percentage of preservative from thermally treated CuNap-treated samples determined by Py-GC/MS revealed that reaction time had a higher impact than temperature (Table 3, Supporting information Table A4 and Fig. A6). The Py-GC/MS results for preservative removal from CuNap-treated wood ties agreed well with our FTIR findings. Light oxygenates, furans/pyrans, levoglucosan, and lignin fractions were fitted to a quadratic model and exposed that temperature had a stronger impact on pyrolytic compounds than other terms (Table 3 and Supporting information Table A5). Therefore, the removal (%) of preservative components from CuNap treated materials and the upgradability of thermally treated wood are important response variables to determine the optimum thermal desorption conditions when a trade-off between preservative recovery efficiency and the quality of thermally treated wood for market demands in downstream thermochemical processes is needed.

Table 6. Pyrolytic compounds produced at 450 ºC from CuNap-treated wood and its thermally treated woods.

RT (min)	Compound		RT (min)	Compound	
4.0	CO_2				
4.2	Methanol	Light Oxy.[1]	28.2	2-Hexadecanol	Nap
4.8	Acetyl ether	Light Oxy.	29.2	Nonadecane	Solvent
5.9	2,3-Butanedione	Light Oxy.	29.2	4-Vinylguaiacol	Lignin
6.2	3-Pentanone	Light Oxy.	30.6	Syringol	Lignin
6.9	Hydroxyacetaldehyde	Light Oxy.	31.6	Hexadecane	Solvent
7.7	Acetic acid	Light Oxy.	32.2	2-Methylhexadecan-1-ol	Nap
8.9	Hydroxyacetone	Light Oxy.	32.5	4-Propenylguaiacol	Lignin
10.7	2-Methylfuran	Furans	32.8	2,5-Dimethoxybenzyl alcohol	Lignin
11.4	Propargyl alcohol	Light Oxy.	33.2	5-Formylguaiacol	Lignin
12.1	Acetoxyacetic acid	Light Oxy.	33.8	Nonadecane	Solvent
12.4	5-(Hydroxymethyl)-2(5H)-furanone	Furans	34.6	Syringaldehyde	Lignin
13.1	2(5H)-Furanone	Furans	35.1	Acetoguaiacon	Lignin
13.6	Butanedial	Light Oxy.	35.9	3,5-Dimethoxyacetophenone	Lignin
14.2	Furfural	Furans	36.1	2-Methylhexadecan-1-ol	Nap
15.9	Acetol acetate	Furans	36.3	Methoxyeugenol	Lignin
16.2	2-Butanone	Light Oxy.	37.9	Nonadecane	Solvent
17.9	2-Hydroxycyclopent-2-en-1-one	Cyclopentanes	38.7	Levoglucosan	Anhydrosugar
18.8	3-Acetyltetrahydro-2-furanone	Furans	38.8	Methoxyeugenol	Lignin
19.8	2(3H)-Furanone	Furans	39.6	Syringaldehyde	Lignin
20.4	3,4-Hexanedione	Light Oxy.	39.9	Nonadecane	Slovent
21.0	3-Methyl-1,2-cyclopentanedione	Cyclopentanes	41.0	Acetosyringone	Lignin
22.5	Guaiacol	Lignin	41.2	Ethyl 2-oxotetradecanoate	Nap
25.4	Homoguaiacol	Lignin	41.7	Heptacosane	Solvent
25.7	Cyclopentyl alcohol	Cyclopentanes	41.8	2-Pentanone, 1-(2,4,6-trihydroxyphenyl)	Nap
26.7	Tetradecane	Solvent[2]	45.2	Heptacosane	Solvent
27.7	4-Ethylguaiacol	Lignin	46.8	Methyl 4-hydroxyoctadecanoate	Nap
27.9	Heptanaldehyde	Nap[3]	48.3	Heptacosane	Solvent
28.0	3-Methyl-2,4(3H,5H)-furandione	Furans			

[1] Light Oxy represents light oxygenated compounds.

[2] Solvent represents diluting solvent compounds in preservative.

[3] Nap represents naphthenic acids.

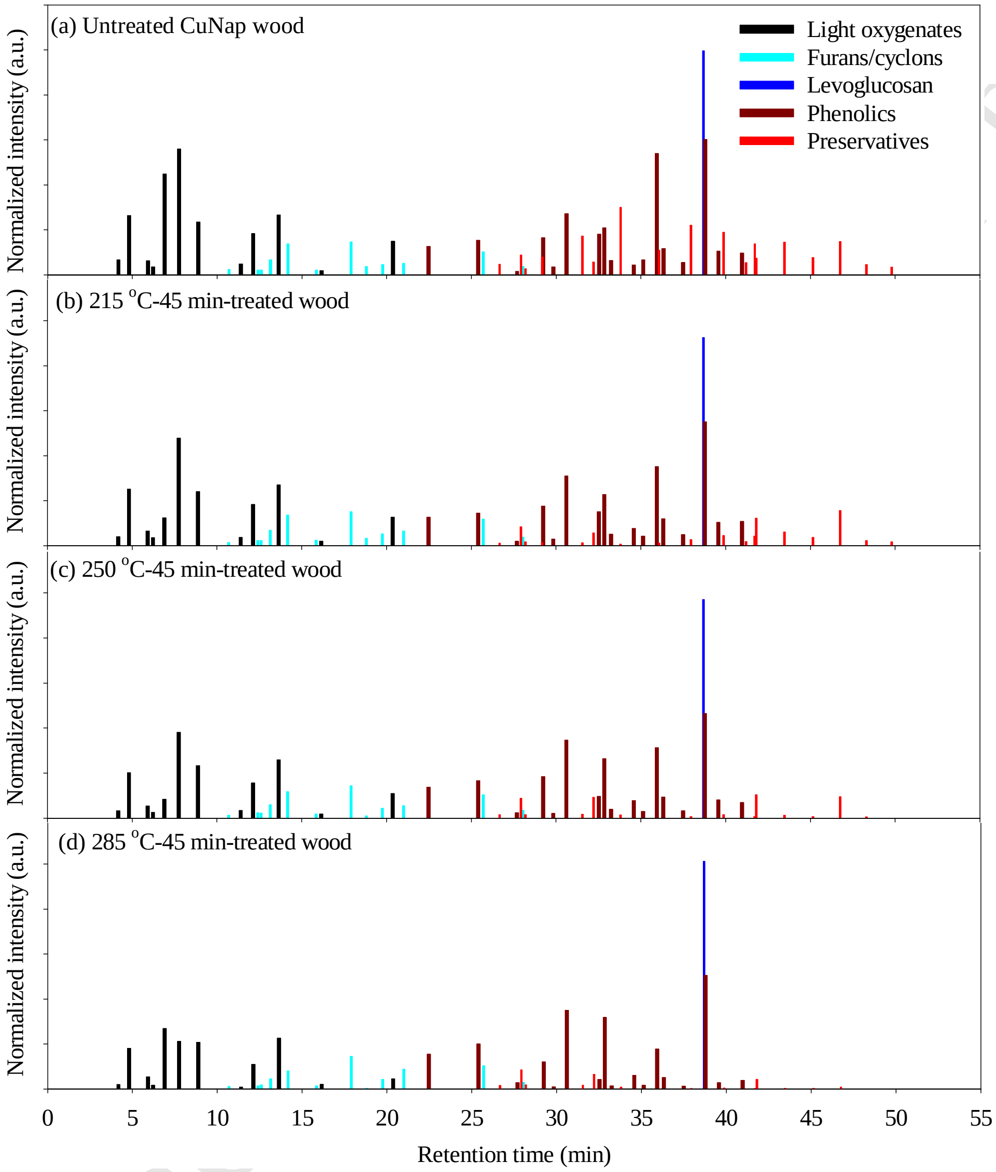


Fig. 3. Representative chromatographic peaks of organic compounds present in untreated and thermally treated wood samples by Py-GC/MS. (a) Untreated CuNap-treated wood, (b) 215 ºC-45 min CuNap treated wood, (c) 250 ºC-45 min CuNap-treated wood, and (d) 285 ºC-45 min CuNap treated wood.

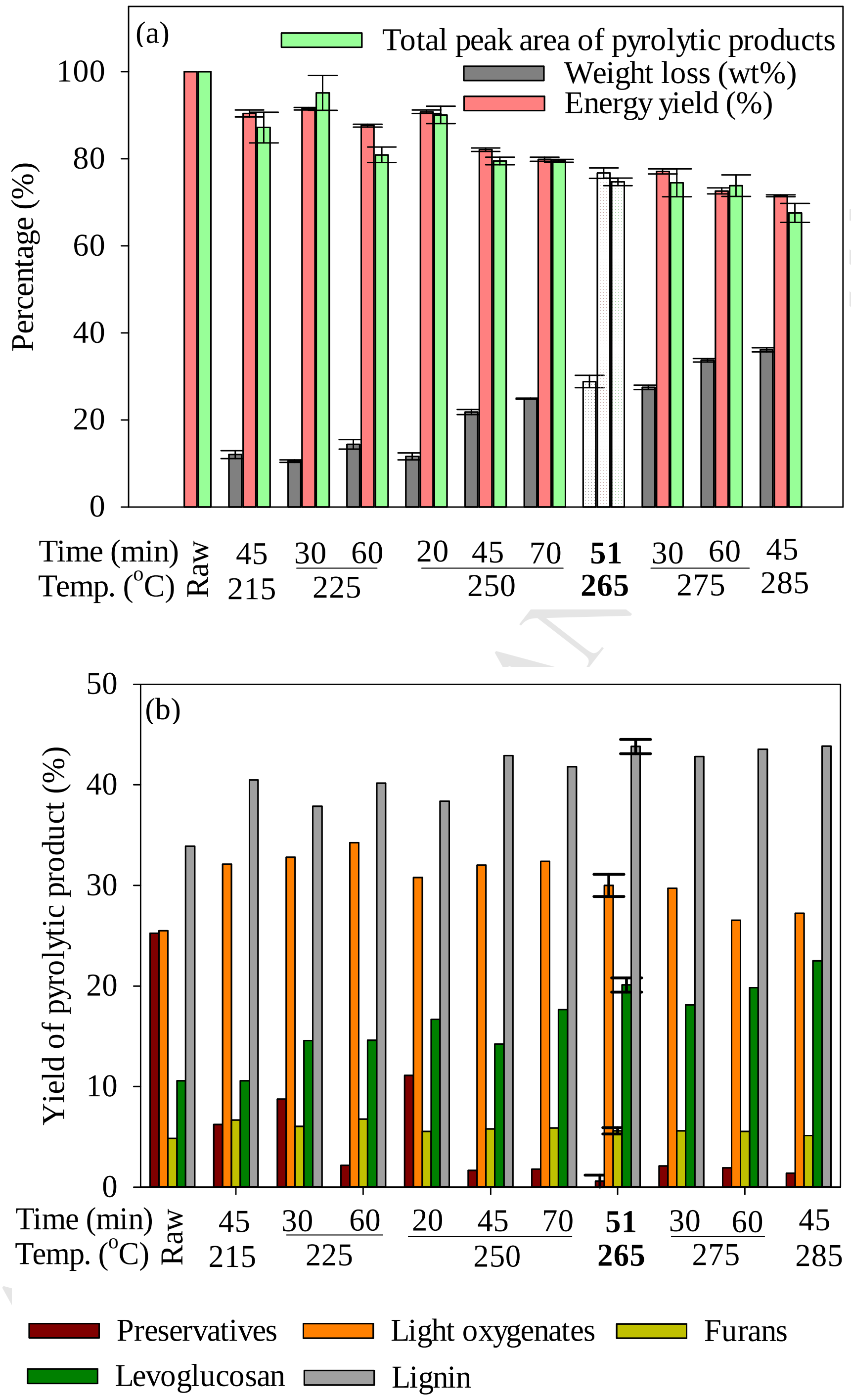


Fig. 4. Weight loss, energy yield, and pyrolytic products at 450 °C of CuNap wood thermally treated under various conditions and predicted optimal conditions (265 °C and 51 min) with 95% confidence interval. (a) Weight loss, energy yield, and total chromatographic peak areas and (b)

pyrolytic products including preservative, light oxygenates, levoglucosan, and lignin-derived compounds.

3.5. Optimization of thermal desorption conditions

Numerical optimization using a prediction profiler function was performed to determine the optimum desorption conditions for maximum recovery of organic preservative from CuNap-treated wood materials. The predicted values for optimization of desorption temperature and reaction time with respect to the maximized recovery (approximately 99 % with confidence interval of 95 %) of preservative were a temperature of 265 ºC (coded level 0.6) and a reaction time of 51 min (coded level 0.4) (Fig. 5). Under these optimal conditions (Fig. 5), a predicted weight loss of 29 % wt took place and the energy yield of the thermally treated wood was 23 % lower than the starting material (Fig. 4a). Furthermore, the predicted total yield of pyrolytic products at the optimum conditions was 25% lower than the untreated CuNap materials (Fig. 4a). The reduction in energy yield and total pyrolytic yield were associated with the desorption of preservative and partial decomposition of the wood matrix under the optimum conditions (Fig. 4a). The distribution (%) of pyrolytic compounds at 450 ºC of wood ties treated at the optimal desorption conditions (265 ºC and 51 min) indicated high quality products with elevated contents of levoglucosan and phenolic compounds, as well as very low preservative content (Fig. 4b). Furthermore, CuNap wood materials treated at the optimum desorption conditions only contained traceable amount of organic preservative components and could be a high quality feedstock for thermochemical processes such as gasification and co-generation. This suggests that treating wood materials at 265 ºC for 51 min improves the quality of the feedstock for thermochemical conversion processes, a treatment similar to that of biomass torrefaction, and revealing the subsequent quality of pyrolytic products (Wang et al., 2016).

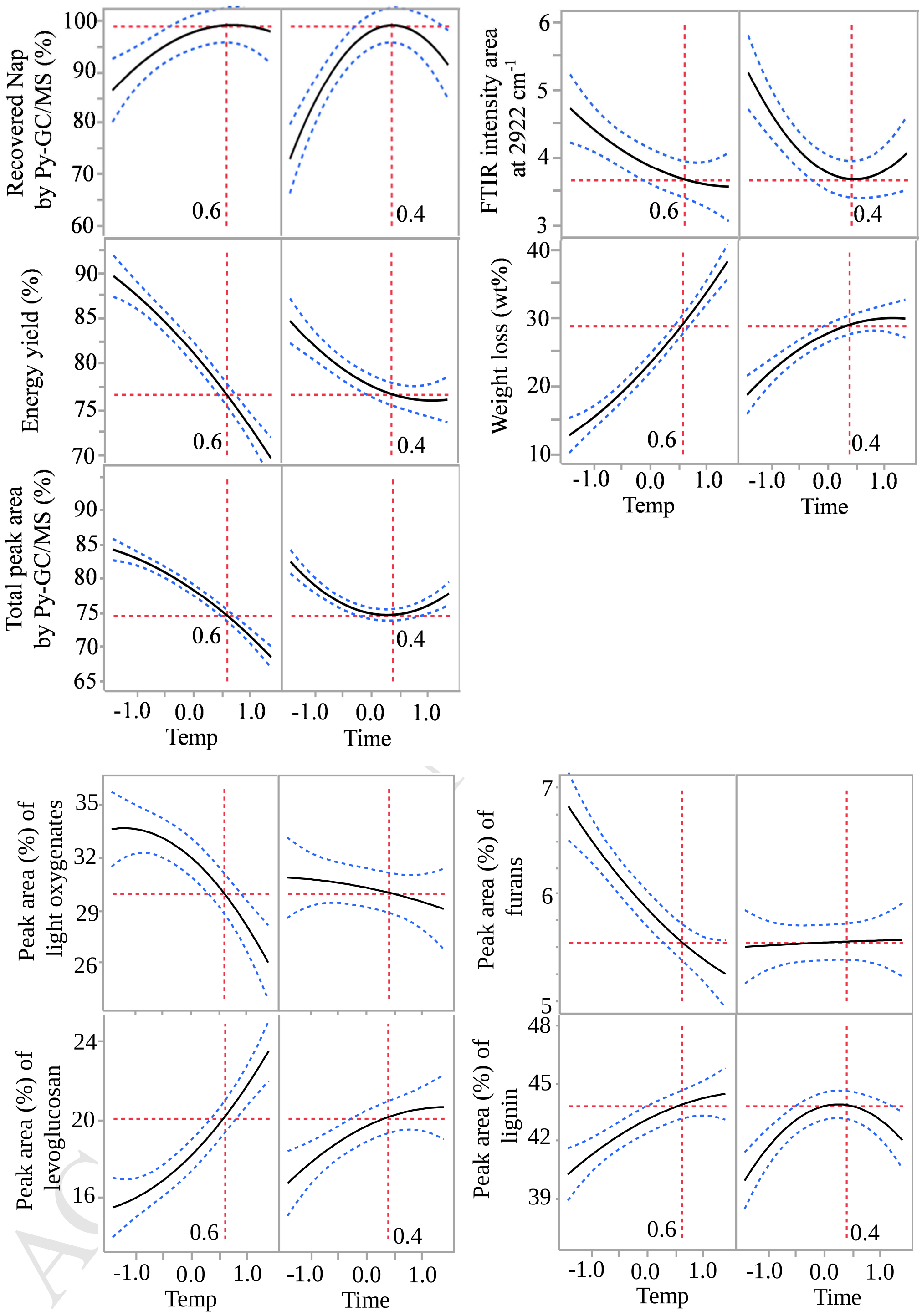


Fig 5. Predicted weight loss, preservative recovery, and yields of pyrolytic products at 450 ºC of the CuNap treated wood thermally treated at the optimum conditions (265 ºC and 51 min). Blue colored dot-line represents confidence interval of 95%. Coded variable of temperature (0.6) and time (0.4) are equivalent to 265 °C and 51 min.

4. Conclusions

The optimum desorption conditions for the maximum recovery of organic preservative components from CuNap-treated wood in a batch-fixed reactor was determined to be at 265 ºC and for 51 min using statistical response surface methodology with a central composite design (CCD) model. The thermal desorption under these optimum conditions predicted a recovery of 95 % of the total organic preservative components. The thermal desorption also generated a high quality biomass with high HHV and low residual preservative. Pyrolysis of the thermally treated solid materials produced higher amount of levoglucosan and lignin-derived compounds than untreated ties. It was concluded that thermal desorption of CuNap treated wood can extract naphthenic acid and carrier oil in the wood which can be reused. Moreover, the processed wood had higher quality than untreated wood and can be used as a feedstock for the production of a variety of fuels and chemicals. The recovery of preservative components together with production of high quality biomass could enable the viability of thermal desorption process for recycling of preservative treated wood. It is hoped that by both capturing the value of preservative components for reuse, and improving the quality of the fuel, the commercial viability of utilizing this otherwise waste material will be significantly improved while avoiding unnecessary landfill or other environmental impacts.

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Highlights

1. Used railroad wood ties were thermally treated for preservative recovery.
2. A response surface methodology identified optimum thermal treatment conditions.
3. A thermal treatment of wood ties recovered 95 % preservative at 265 °C and 51 min.
4. Preservative-free woods contained 21.9 MJ/kg HHV and 77 % energy yield.
5. Pyrolysis of thermally treated wood improved levoglucosan and phenolics yields.