Thermal desorption of creosote remaining in used railroad ties:
Investigation by TGA and Py-GC/MS

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Abstract

A two-step thermal process, an initial thermal treatment at mild temperature followed by a fast pyrolysis step, was investigated to recover wood preservatives and produce preservatives-free wood for production of high quality bio-oil from used creosote-treated railroad ties. During the initial thermal treatment at temperature of 280 °C for 10 to 30 min, the treated wood ties underwent a 20 – 25 % weight loss with energy yield (77 - 83 %). Energy yield at 280 °C was lower than that at 200 and 250 °C (92 – 97 %) but higher than that at the 300 °C (64 – 74 %). Recovery level of creosote at 280 °C was comparable to that at 300 °C. Fast pyrolysis at 450 °C of the 280 °C-treated wood ties produced high amount of levoglucosan and phenolic compounds with a traceable amount (1.7 – 1.9 % of the total peak area) of creosote compounds.

Keywords: creosote; fast pyrolysis; used railroad ties; thermal desorption; wood preservatives.

1. Introduction

In the USA, the total number of railroad ties (crossties or sleepers) in the track accounts for approximately 700 – 800 million. Over 21 million railroad ties are produced per year with approximately 20 million being replaced after providing excellent primary service in railroad track [1, 2]. Over 95% of the railroad ties produced are made from wood and thus they are prone to biological and physical deterioration. To address this challenge, the ties are pressure-treated with preservatives, such as creosote and copper naphthenate (CuNap). Approximately 98 % of all wood crossties produced in the U.S. are treated with the aforementioned preservatives. Creosote is a restricted use pesticide only allowed for application to industrial commodities and applied under special license. The U.S. Environmental Protection Agency (U.S. EPA) has determined that creosote, a mixture of 200 – 250 identifiable chemicals including 85 % of polycyclic aromatic hydrocarbons (PAHs), is a probable human carcinogen [3]. Approximately 9 kg of creosote is impregnated in about 0.1 m³ of wood tie [4] and about 65 % of the total creosote remains in wood ties after 35 years of service [5]. This loss of preservatives is due to volatilization, weathering, and biological and photo-chemical degradation that take place mostly on the surface of the ties. After their primary use in track, used railroad ties are re-used in track (0.9 %), used as commercial and residential landscape timbers (18.0 %), and especially utilized as fuel in approved boiler and gasification facilities (81.3 %) [6]. Only a small percentage of used railroad ties is currently disposed of in landfill (0.3 %).

Many industrial boilers, such as the pulp and paper industry, have an ideal fuel source in the form of used treated wood from the railway industry. However, the recent classification of treated wood as waste by the U.S. EPA, under their Non Hazardous

Secondary Materials (NHSM) rule, will deter the use of treated wood as fuel. Starting from 2016, used railroad ties, which have provided economic source for energy, will be disposed of, via incineration or in landfill [7]. The Treated Wood Council (TWC), a trade group representing wood traders and preservatives suppliers, has petitioned the U.S. EPA for a categorical exemption from this rule. However, even if successful, current used wood ties utilization in boilers remains a challenge due to increasing emissions standards for boilers and the low cost of natural gas.

Used wood railroad ties generally have a high hydrocarbon content, are relatively dry and therefore have higher calorific value (29 MJ/kg) than most biomass feedstocks [4]. These advantages make them suitable for conversion via thermochemical processes such as pyrolysis, gasification, and combustion. Pyrolysis has an edge over other thermochemical conversion processes as it diversifies the product portfolio while affording higher thermal efficiency due to lower operating temperatures [8]. Pyrolysis is a thermochemical process employed to convert biomass in the absence of oxygen at operating temperatures ranging between 450 and 600 °C. Conventionally, pyrolysis is used to directly convert biomass into bio-oil, biochar, and noncondensable gases. Subsequently, bio-oil can be upgraded to biofuels and chemicals while non-condensable gases can be used for combined heat and power (CHP). Additionally, biochar can be utilized as a soil amendment or alternatively can be burnt for CHP as a bio-coal [9, 10]. Therefore, in addition to CHP, conventional pyrolysis of used railroad ties will allow to produce intermediate products for bio-products and biofuels, if wood preservatives can be extracted separately while retaining other desirable qualities of the wood. A few groups have tried to make preservatives from pyrolytic bio-oil [11] or to pyrolyze used railroad ties to produce bio-oils [12], but in general either approach

109 produces a contaminated bio-oil that is difficult to separate or a less effective non-
110 registered preservatives system including wood-derived contaminants. Therefore, the
111 objective of this study was to investigate a two-step thermal process that differs from
112 the conventional approach by preceding the pyrolysis step with a customized thermal
113 desorption step that addresses specific challenges associated with used wood ties
114 containing hazardous preservatives. The thermal desorption step will enable the
115 removal and recovery of the preservatives prior to the fast pyrolysis step. The ability to
116 recover preservatives may provide an added new advantage via our two-step process
117 with the potential of re-using recovered preservatives to treat new wood ties.
118 Thermogravimetric analysis (TGA) was used to estimate the weight loss during the
119 thermal desorption step and analytical pyrolysis-gas chromatography/mass
120 spectrometry (Py-GC/MS) was used to identify optimum temperature to perform the
121 desorption, to semi-quantify the recovery of wood preservatives, and to evaluate the
122 upgraded wood ties for subsequent fast pyrolysis for bio-oil production.

123

2. Materials and methods

2.1 Materials

A used creosote-treated railroad tie (red oak, *Quercus rubra*) was obtained from Nisus Corp. (Rockford, TN, USA). The tie was ground into less than 0.425 mm particle sizes with a knife mill before testing.

2.2. Methods

2.2.1 Physical characterization

The used creosote-treated railroad tie sample was characterized by the following analytical techniques. Proximate analysis, including moisture content, ash content, volatile matter, and fixed carbon, of the raw sample was measured following the ASTM D 1762-8. Ultimate analysis, including carbon, hydrogen, and nitrogen, was measured using a CHN analyser (2400 Series II CHNS/O, PerkinElmer). Moisture content was also measured using the Karl Fischer titration method. Briefly, 30 mL of a 2:1 (v/v %) mixture of methanol: chloroform were placed in the titration vessel and titrated to dryness (conditioned). Then, approximately 0.2 g of material was added and the water content was titrated using hydranal composite 5K solution. Inorganic elements were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 7300 DV spectrometer, PerkinElmer) after acid microwave digestion of the material [13]. All experiments were performed in triplicate.

2.2.2 Thermogravimetric analysis

A thermogravimetric analyzer (Pyris 1 TGA, PerkinElmer) was employed to monitor weight loss as a function of temperature and to evaluate thermal decomposition of the wood ties over time. 9 - 10 mg of the sample were heated from 30 to 200, 250, 280 or

300 °C at a rate of 10 °C/min and held for 10, 20 or 30 min, and then cooled down to less than 30 °C under nitrogen gas flow (20 mL/min). In order to evaluate the effect of desorptive temperatures on the wood ties, the thermally treated samples were then heated from 30 to 800 °C at 10 °C/min (nitrogen gas flow, 20 mL/min), held for 10 min at 800 °C to collect thermal decomposition curves. Final solid yield (biochar) was determined at 800 °C under nitrogen gas flow. Ash content was measured by switching nitrogen gas to air flow at 800 °C and holding for 30 min. The thermal characteristics were described by TG and differential TG (DTG) curves. The 200, 250, 280 and 300 °C-treated samples were analyzed using the CHN analyzer for compositional distribution of carbon, hydrogen, nitrogen, and oxygen. All experiments were performed in triplicate. The higher heating value (HHV) of each thermally treated sample was calculated using an ordinary least-squares regression method [14]. Energy yield (%), defined as the amount of energy conserved in the solid part after the initial thermal treatment, was calculated by equations 1 and 2 as follows [15].

$$Mp = \frac{Mt}{Mo} \times 100 (\%) \quad (\text{eq. 1})$$

$$\text{Energy yield } (\%) = \frac{(Mp \times Ht)}{Ho} \times 100 \quad (\text{eq. 2})$$

where, Mp = weight yield (%); Mt = weight of thermally treated sample; Mo = weight of raw sample; Ht = HHV of thermally treated sample; Ho = HHV of raw sample.

2.2.3 Pyrolysis-gas chromatography/mass spectrometry

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was used to simulate the proposed two-step thermal process. A Perkin Elmer Clarus 680 Gas Chromatograph coupled with a Clarus SQ 8C Mass Spectrometer and fitted with a micro-pyrolyzer and an autosampler that loads samples for pyrolysis (Frontier EGA/Py-3030 D) was used.

Sample pans were layered with 0.4 mg of material and were dropped via the autosampler into the pyrolysis furnace that was directly attached to the injection port of a GC/MS instrument. For the initial thermal desorption step, the furnace was held at 200, 250, 280 or 300 °C for 10, 20 or 30 min residence time to desorb the preservatives components present in the sample. At the conclusion of this time, the sample was raised and maintained at room temperature under helium gas condition. Simultaneously, the vapor was swept into the GC-injection port (temperature 270 °C) by the GC carrier gas (helium, 1mL/min) that passes through the furnace. The vapor was then separated using an Elite 1701 MS capillary column (60 m x 0.25 mm ID x 0.25 micron film thickness), and analyzed using MS (source temperature 270 °C, 70 eV electron ionization). After the GC/MS analysis was completed, the furnace was heated to 450 °C for the second step, the fast pyrolysis. The thermally treated sample was dropped again into the furnace and pyrolyzed at 450 °C for 12 s. The vapor was injected into GC/MS for gas analysis. Four pyrograms per sample were collected. Chromatographic peaks were extracted from the pyrograms by peak height to noise ratio set at ≥ 10 and compared to the NIST library of fragmentation patterns for the identification.

3. Results and discussion

3.1. Thermogravimetric analysis

The creosote-treated wood tie sample was thermally treated at three different isothermal temperatures (200, 250, 280 or 300 °C) for 10, 20 or 30 min to desorb creosote by TGA (Fig.1). The TG curves of the sample demonstrated a first weight loss from 40 to 110 °C (under 10 min) and then had a second weight loss starting at 110 °C at the different isothermal conditions (Fig. 1a). The initial weight loss at 110 °C indicates the removal of water and degradation of creosote present in the tie sample, which collaborated the difference found between weight loss (7.7 wt%) observed at 105 °C for 24h in the oven (traditional method to measure moisture content in wood) and water content (5.7 wt%) measured by Karl Fisher titration (Table 1). The second weight loss at isothermal steps at residence time of 10, 20, and 30 min was 7.6 - 8.0 wt% at 200 °C, 12.6 – 15.9 wt% at 250 °C, 21.6 - 28.0 wt% at 280 °C, and 31.9 – 42.4 wt% at 300 °C (Fig. 1b). This result is in accordance with Becker et al. [16] who demonstrated that the degradation of creosote starts with a drying process of the wood around 75 °C. As heating temperature increases, the wood matrix is decomposed; the resulting products and creosote compounds with different boiling points ranging from 180 to 400 °C are gradually observed.

Insert Fig. 1 here

Insert Table 1 here

Although the net effect of the residence time was not as pronounced as the reaction temperature, the weight loss drastically increased with residence time at temperature above 280 °C, resulting in a lower solid product yield. In order to compare the degree of structural decomposition of the wood tie sample, the raw and thermally treated tie

samples by different temperatures and times were analyzed using again TGA from 30 to 800 °C at 10 °C/min (Fig. 2). The TG thermogram of the 200 °C-treated sample (Fig. 2a) still exhibited a 3.0 wt% weight loss at around 110 °C, whereas higher temperature-treated samples had less than 1.3 wt% of weight loss. This weight loss after thermal desorption treatment at low temperatures suggests that creosote compounds are still present in the thermally treated tie samples and that the temperature was not high enough to completely desorb these compounds. The TG thermograms also exhibited a shift of initial degradation temperature at which drastic weight loss starts, toward higher TG temperatures for elevated thermally treated tie samples. This shift coincides with the fact that wood components such as hemicellulose, cellulose, and lignin, begin to decompose at higher temperature [17]. The derivative TG (DTG) curves (Fig. 2b) present the thermal decomposition peaks corresponding to the temperature at which the weight loss rate is maximized. The DTG curves of the 200 and 250 °C-treated tie samples closely overlapped with the raw tie sample with a shoulder peak at around 305 °C and a major peak at 352 °C, suggesting that treatment at temperature lower than 250 °C does not significantly affect the wood components. However, the DTG curve of the 300 °C-treated tie sample had a single DTG peak at around 352 °C with no shoulder peak at 305 °C. The absence of this shoulder may be attributed to significant degradation of hemicellulose and cellulose during the thermal desorption treatment at 300 °C. In general, wood components thermally decompose under various temperature ranges: hemicellulose breaks down in the temperature range of 220 – 315 °C; cellulose between 240 and 360 °C; and lignin from 250 to 500 °C [18]. The end solid product (biochar yield) obtained at 800 °C of thermally treated samples gradually increased with thermal desorption temperatures and residence time (Fig. 2c). This result indicates

that a degradation of hemicellulose and cellulose and the resulting high lignin content in the elevated heat-treated tie sample induces high biochar yield by cross-linkage reactions during lignin pyrolysis [19].

Insert Fig.2 here

3.2. Elemental analysis

Elemental components such as carbon(C), hydrogen (H) and oxygen (O) of the wood tie sample indicated that increasing reaction temperature and residence time augmented the carbon content while reducing the hydrogen and oxygen content (Fig. 3a). It is worth noting that these percentages are relative values that are derived from a greater reduction in oxygen and hydrogen than carbon in the wood tie sample. Higher weight loss with elevated temperatures and longer residence times translated into a greater loss of volatile matter, which included creosote compounds, cellulose and hemicellulose present in the tie wood as evidenced in Fig. 2a.

A plot of the molecular ratios of carbon, hydrogen and oxygen (atomic H/C versus O/C ratios) on the van Krevelen diagram demonstrated that atomic hydrogen, and oxygen content linearly decreased with increasing reaction temperature and residence time (Fig. 3b). Temperature above 280 °C had a dominant influence on the reduction of molecular ratios of H/C and O/C, indicative of removal of creosote compounds and thermal degradation of wood components. Residence time also reduced hydrogen and oxygen content at temperature above 250 °C.

Thermal treatment above 250 °C clearly led to a substantial increase in the HHV, while residence time had a less significant impact (Fig. 3c). This increase in the HHV with temperature and residence time is mostly due to a reduction of both, water and volatile

matter including creosote and wood degradation products. The production of water molecules by dehydration reaction results in a decrease of hydrogen and oxygen content from the wood tie without reduction of carbon content.

The effect of reaction temperature and residence time on the energy yield of the heat-treated wood tie sample was observed in Fig. 3c. The calculated energy yield is a function of weight yield and the HHV at specific thermal treatment conditions. The overall decrease in energy yield is due to an increase in HHV while a reduction of the weight yield takes place with the thermal treatment implying that the increase in the HHV is not sufficient to compensate for the weight loss with high temperatures. Energy yield gradually decreased with reaction temperature from 200 to 250 °C and drastically dropped down above 280 °C. A longer residence time at temperature above 280 °C also significantly affected the energy yield. The energy yields, ranging from 74 to 77 % at residence time of 20 and 30 min at 280 °C and for samples exposed to 300 °C for 10 min, dramatically decreased to 69 % at residence time of 20 min and 64 % after 30 min at 300 °C, which indicates that the effect of residence time above 280 °C is as prominent as that of reaction temperature. This demonstrates that significant weight loss with longer residence time at high temperature is caused by the partial volatilization of creosote compounds and decomposition of hemicellulose, cellulose and lignin. The thermal treatment to desorb preservatives from wood ties is similar to a torrefaction process of biomass that usually occurs at 200 – 300 °C under an inert environment to upgrade the fuel quality of biomass for thermochemical conversion [17].

Insert Fig. 3 here

3.3. Pyrolysis-GC/MS analysis

3.3.1. Thermal desorption of creosote present in wood ties

The two-step thermal process consisting of a thermal desorption step of creosote and a subsequent fast pyrolysis step, was conducted using an analytical pyrolysis-GC/MS system to monitor the effect of reaction temperature and residence time on creosote desorption and thermal decomposition of the wood matrix. The initial thermal desorption step mimicked the TGA experiments and was performed at 200, 250, 280 or 300 °C for 10, 20 or 30 min of residence time (Pyrograms and identified fragments can be seen in Supporting information Fig. A.1. and Table 2, respectively). The peak areas of 50 identified compounds in the pyrograms were categorized as creosote, anhydrosugars, phenols, furans, and light oxygenates to primarily estimate the yield changes of these volatile organic products produced under different thermal desorption treatment conditions (Table 2 and Fig. 4). The peak areas of these compounds were added to assess the total chromatographic signal in function of temperature and time (Fig. 4a). Although the effect of the residence time was not as prominent as the temperature, both parameters affected the amount of organic volatiles produced. Total peak area increased when temperature was raised from 200 to 300 °C for a residence time of 30 min. The impact of residence time on volatile products was more pronounced for temperature ≥ 280 °C. The increase of total peak area was correlated to the weight loss (wt%) with increasing temperature and residence time in the TGA experiment (Fig. 1). An increase of peak area through partial decomposition of the wood matrix at temperature above 280 °C produced larger amounts of anhydrosugars and phenolic compounds (Fig. 4a).

The chromatographic peak area of creosote compounds (Table 2) produced during the thermal desorption process was extracted from the pyrograms and a total of 21 individual creosote compounds were detected and identified. The distribution of these compounds pointed out that ten major PAHs compounds were predominant in the creosote vapor and their amount increased with temperature and residence time including naphthalene, acenaphthene, methylnaphthalene, fluorine, phenanthrene, fluoranthene, anthracene, dibenzofuran, benzanthracene, and pyrene (Fig. 4b). The chromatographic peak area exhibited no change at 200 °C with varying time, however, a significant increase in these compounds occurred at 250 and 280 °C followed by a continuous increase at 300 °C. Longer residence time at 250 and 280 °C also produced larger amount of creosote compounds. The total amount of creosote released from the thermal desorption step at 300 °C for 30 min and the one step fast pyrolysis at 450 °C and 12s was comparable (Fig. 4b). These results suggest that the thermal desorption occurring between 280 and 300 °C for a longer residence time is beneficial to volatilize most of the preservatives compounds present in creosote-treated wood ties. At the same time, higher temperature and longer residence time degraded the wood matrix. The fraction of wood-decomposed products generated by the thermal desorption at 200 °C was mostly anhydrosugars derived from carbohydrates and a small fraction of phenolic compounds produced from lignin, although the total peak area was very low as it can be seen in Fig. 4a. As temperature and residence time increased from 250 to 300 °C and from 10 to 30 min respectively, a dramatic increase in anhydrosugars and a gradual increase in phenolic compounds was observed (Fig. 4a). This can be explained by the fact that hemicellulose and cellulose are relatively more temperature sensitive than lignin, which induces higher thermal degradation rates for these carbohydrates.

Temperature above 250 °C degrades hemicellulose, cellulose and lignin into smaller compounds such as anhydrosugars, furans, light oxygenated compounds, and phenols through fragmentation and depolymerization reactions [20]. These results are detrimental in determining optimal conditions to thermally desorb creosote and its maximum recovery. In addition to creosote recovery, the thermal desorption step should upgrade or at least not significantly reduce the quality of the wood that will make it suitable for thermochemical conversion such as pyrolysis, combustion, or gasification thereby reducing PAHs emission in the environment. Therefore, the quality of the thermally treated wood ties as a potential upgraded feedstock for producing bio-oil via a fast pyrolysis step using Py-GC/MS was estimated in the next section.

Insert Fig. 4 here

3.3.2. Fast pyrolysis of thermally desorbed railroad ties

The thermally treated wood tie samples under different temperatures and residence times were subsequently pyrolyzed at 450 °C for 12 s using the same Py-GC/MS system. The generated pyrograms and peak identification are provided in Fig. A1 and Table A1, respectively. The analyses of the fast pyrolysis step data indicated a gradual reduction in the total peak areas of organic volatile products produced from the thermally treated wood tie samples with temperature and residence time (Fig. 5a). This could be explained by a decrease in the pretreated sample weight through the initial thermal desorption step and an increase of biochar product via the formation of additional cross-linkage in the thermally treated sample as demonstrated by the TGA experiments (Fig. 2). Total peak areas for creosote compounds produced during the

pyrolysis step were significantly reduced after the thermal desorption step (Fig. 5a and 5b). For example, the vapor of the fast pyrolysis of the 200 °C-treated wood tie contained only 4.7 - 5.9 % creosote (Fig. 5c), which was a significant reduction compared to 15.0 % creosote produced from the untreated (raw) wood tie sample. Pyrolysis of the above 250 °C-treated wood ties produced only traceable residues (1.3 – 1.9 % creosote peak of the total peak area) of creosote compounds with relatively high boiling point such as fluorine, dibenzofuran, phenanthrene and fluoranthene (Fig. 5b and 5c). The distribution (%) of organic compounds (Fig. 5c) showed that the pyrolytically volatile products produced from the 200 °C-treated wood tie had similar distribution to the untreated wood tie, which is due to minimum degradation (weight loss) of the wood components and the not complete desorption of creosote during the low thermal desorption step. The level of anhydrosugars, especially levoglucosan, increased until temperature reached 280 °C. A decrease in these components was observed at 300 °C while phenolic compounds which derived mostly from lignin increased with time at 300 °C. The amount of furans and light oxygenated compounds gradually decreased with temperature. These results indicate that pyrolysis of wood tie that was thermally pretreated at higher temperature and longer residence time produces vapor containing more levoglucosan and lignin-derived compounds. Many researchers [21-23] have reported that torrefaction of biomass at 200 – 300 °C reduces hemicellulose content in biomass, which lowers the amount of small molecular compounds such as acetic acid, acetol, and furfural in the subsequent pyrolysis bio-oil and enhances the decomposition of cellulose into anhydrosugars such as levoglucosan. Based on our findings, pyrolysis of thermally preservatives-free railroad ties will

produce high quality of bio-oils with low water content and acidity, high pyrolytic lignin and levoglucosan.

It is important to consider the trade-off between creosote recovery (%) and energy yield (%) of the pretreated ties for a subsequent thermochemical conversion, and decide on thermal desorption conditions including temperature and residence time. The thermal desorption temperature at 200 °C, although resulting in a high energy yield (90 – 92 %), did not produce a biomass with high HHV values nor high creosote desorption level. On the other hand, thermal desorption at 300 °C produced a lower energy yield (64 – 74 %) and caused an increase in the HHV (20.3 – 20.7 MJ/kg) and a dramatic desorption of creosote from the used wood tie. The intermediate thermal desorption temperature at 280 °C for 10 to 30 min of residence time appeared to provide a compromise, as it produced HHV values of 19.7 – 19.9 MJ/kg and energy yield between 77 and 83 % while maintaining a similar creosote desorption yield with that of the thermal desorption temperature at 300 °C. In addition to an increase in the HHV and the creosote recovery from the wood tie, 280 °C-treated wood ties contained only low traceable creosote residue and through the desorption step became an upgraded feedstock for fast pyrolysis to produce high quality bio-oil containing higher level of levoglucosan and lignin-derived compounds and lower water content and acidic compounds.

Insert Fig. 5 here

4. Conclusions

A two-step thermal process of preservatives-treated wood would be a good alternative technology for the re-use of railroad ties. It would produce renewable energy and chemicals, reducing negative environmental impacts including continued release of hazardous pollutants if they were disposed of in landfill. Future work will look at larger scale extraction of preservatives using an initial heat treatment at 280 °C. The recovered preservatives can be re-used to treat new ties in order to offset the cost of the thermal desorption step and that the preservatives-free wood be used for production of high quality bio-oils or as boiler fuel.

435 **Acknowledgements**

436 The authors would like to thank the support of the 2014-2015 AgResearch Innovation
437 grant (the University of Tennessee Institute of Agriculture), USDA Agriculture and
438 Food Research Initiative (AFRI, Grant # 2015-6021-24121) and Nisus Corporation
439 (Rockford, TN, USA) for this work.

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Fig. 1. Thermal desorption treatment of creosote-treated wood tie samples at 200, 250, 280 or 300 °C for 10, 20 or 30 min of residence time by TGA. (a) TG thermograms of different thermal treatments and (b) weight loss % by the thermal treatments.

Fig. 2. Representative thermogravimetric data of the raw and thermally treated wood tie samples at 200, 250, 280 or 300 °C for 10 min residence time using a TGA temperature ranging from 30 to 800 °C at a heating rate of 10 °C/min with nitrogen flow. (a) TG thermograms of the thermally treated samples, (b) DTG curves of the heat-treated samples, and (c) biochar yield (wt%) at 800 °C.

Fig. 3. Elemental analysis of the wood tie sample treated at 200, 250, 280 or 300 °C for 10, 20 or 30 min residence time. (a) Carbon, hydrogen and oxygen content, (b) Van-Krevelen diagram, and (c) Average higher heating value (HHV) and energy yield (%).

Fig. 4. Total chromatographic peak areas of organic volatile products produced from the creosote-treated wood tie during the thermal desorption process condition, 200, 250, 280 or 300 °C for 10, 20 or 30 min residence time using Py-GC/MS. (a) Total chromatographic peak areas of organic volatile compounds and (b) total peak areas of individual creosote compounds.

Fig. 5. Total chromatographic peak areas of organic volatile products produced from the thermally pretreated wood samples during the fast pyrolysis step at 450 °C for 12 s residence time using Py-GC/MS. (a) Total chromatographic peak areas of organic volatile compounds, (b) Total peak areas of individual creosote compounds, and (c) Total peak areas of carbohydrates- and lignin-derived compounds.

717 **Table 1.** Properties of used creosote-treated railroad tie samples.
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Proximate analysis (wt%)									Ultimate analysis (wt%)							
¹ Moisture content (wt%)			² Moisture content		Volatile matter	Ash	Fix carbon		C	H	N	³ O				
5.7			7.7		80.6	0.5	18.9		46.6	6.1	0.1	47.2				
(0.1)			(0.3)		(0.3)	(0.0)	(0.3)		(0.1)	(0.2)	(0.0)	(0.1)				
Inorganic element (mg/kg on dry basis)																
Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Sr	Ti	Zn	P	S	Si
49	13	897	4	7	495	1041	113	25	306	296	17	14	20	172	339	6594
(5)	(1)	(36)	(0)	(1)	(68)	(43)	(11)	(1)	(25)	(49)	(2)	(3)	(6)	(24)	(41)	(271)

¹) Moisture content measured by Karl Fisher titration method
²) Moisture content measured by weight difference at 105 °C
³) Oyxgen was calculated by difference (100-C%-H%-N%-ash %)

719
720
721
722
723

Table 2. Organic volatile compounds identified from the creosote-treated wood tie samples produced by the thermal desorption process at 200, 250 or 300 °C for 10, 20 or 30 min residence time by Py-GC/MS.

No.	Compound	RT (min)	No.	Compound	RT (min)
1	Furfural	10.5	26	p-Propylguaiacol	33.9
2	Pentanedioic acid	17.2	27	Fluorene	34.4
3	2H-Pyran-2,6(3H)-dione	19.8	28	3',5'-Dimethoxyacetophenone	35.3
4	Phenol	20.9	29	2-Hydroxyfluorene	35.4
5	o-Guaiacol	21.4	30	Hydroxyisoeugenol	36.6
6	2,4-Hexanedione	21.6	31	2-Allyl-1,4-dimethoxy-3-methyl-benzen	37.7
7	2-Deoxy-D-galactose	21.7	32	Levoglucosan	38.1
8	Naphthalene	23.2	33	Methoxyeugenol	38.2
9	Levoglucosenone	24.3	34	Dibenzothiophene	38.6
10	d-Mannose	24.7	35	Syringaldehyde	38.9
11	DL-Arabinose	24.7	36	Phenanthrene	39.3
12	Quinoline	25.8	37	Anthracene	39.5
13	1-Methylnaphthalene	26.4	38	Homosyringic acid	39.8
14	2,4-Hexanedione	27.1	39	Acetosyringone	40.3
15	1,3-Di-O-acetyl- α - β -d-ribose	28.5	40	1-Methylanthracene	41.5
16	Biphenyl	28.7	41	1-Methylphenanthrene	41.6
17	1,7-Dimethylnaphthalene	29.4	42	Benzo[def]fluorene	42.0
18	5-Hydroxymethylfurfural	29.6	43	2-Phenylnaphthalene	42.8
19	Syringol	30.3	44	Dibenzopyrrole	42.9
20	Acenaphthene	31.7	45	Fluoranthene	45.2
21	Isoeugenol	31.9	46	3,5-Dimethoxy-4-hydroxycinnamaldehyde	46.0
22	Sucrose	32.0	47	Pyrene	46.2
23	1,2,4-Trimethoxybenzene	32.2	48	1-Methylpyrene	47.7
24	Vanillin	32.5	49	Benzo[l]phenanthrene	52.3
25	Dibenzofuran	32.7	50	Benzanthracene	52.5