Recovery of creosote from used railroad ties by thermal desorption

Pyoungchung Kim^{1*}, Jeff Lloyd², Jae-Woo Kim², Nourredine Abdoulmoumine³ and Nicole Labbé^{1*}

¹ Center for Renewable Carbon, the University of Tennessee, 2506 Jacob Dr., Knoxville, TN 37996, USA

² Nisus Corp., 100 Nisus Dr. Rockford, TN 37853, USA

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

*Corresponding authors.

Pyoungchung Kim: pkim1@utk.edu, Phone: (865) 974-5086. Fax: (865) 946-1109

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

Abstract

Used creosote-treated wood ties were thermally treated between 250 and 350 °C to recover preservative and upgrade the wood to provide an improved quality biomass for thermochemical processes. With thermal treatments ranging from 250 to 300 °C, the amounts of creosote, mostly consisting of polycyclic aromatic hydrocarbons (PAHs), recovered were from 47 to 79 % of total creosote present in the used ties. Thermal treatment at 350 °C recovered 97 % of total PAH compounds. Larger amounts of PAHs with higher molecular weights (HMWs) and lower vapor pressures (LVP) were recovered at elevated temperatures. Temperature above 300 °C decomposed the wood matrix, with a mass loss ranging between 50 to 63 wt% and produced large amounts of light organics, anhydrosugars, and phenolic compounds that would contaminate the recovered creosote. Our study concluded that thermal treatment ranging between 275 and 300 °C would be preferred to recover preservative for recycling and improve the wood quality,

i.e., high carbon content and caloric value, and low hazardous pollutants (creosote residues) for thermochemical processes such as pyrolysis or gasification. These findings suggest that the proposed approach could be a commercially viable and environmentally beneficial alternative to landfill for used railroad ties.

Keywords:

Creosote; Thermal desorption; thermochemical processes; used railroad ties; polycyclic aromatic hydrocarbons.

1. Introduction

Creosote is a fungicide and insecticide used as a wood preservative and primarily to treat railroad ties, utility poles, piling and bridge timbers to provide long-term resistance to biodegradation. Creosote is a distillation product of coal tar derived by the high temperature carbonization of bituminous coal [1]. It is a complex mixture typically composed of approximately 85% polycyclic aromatic hydrocarbons (PAHs) and 2 – 17 % phenolics, the composition of which varies across sources and manufactures [2]. The U.S. Environmental Protection Agency (EPA) has determined that approximately 20 – 40 % of the total weight of creosote can be attributed to sixteen PAHs, which are priority pollutants and potential carcinogens such as benzo[a]pyrene [3].

In the U.S., there are 700 – 800 million railroad ties in service in railroad tracks with approximately 20 million ties being replaced annually [4]. Over 95% of railroad ties produced are wood ties treated by impregnation with creosote and coal tar, or creosote and oil blends [4]. On average, 88 kg/m³ of creosote is impregnated into a wood tie and 65 % of the creosote are

still retained after 35 years of typical service [5]. After their service life, over 80 % of used wood ties are repurposed as fuel for industrial wood-fired boilers and gasification facilities to produce combined heat and power [6]. However, under the U.S. EPA's 2014 NHSM (Non Hazardous Secondary Materials) rule, treated wood such as railroad ties are newly classified as waste [7]. As a result, many treated wood ties previously used as biomass fuel will be landfilled. In addition to the considerable landfill space that will be required to dispose of used ties, landfill-disposed biomass produces greenhouse gases (GHG) such as carbon dioxide and methane [8].

As an alternative to landfilling, a few research groups have used fast pyrolysis to produce a liquid fraction containing creosote and wood-decomposed bio-oil as a bio-oil preservative [9], which is problematic as the mixture is not EPA registered and is difficult to separate into intermediate sources for chemicals, fuels, and biomaterials [10]. In our previous study [11], we demonstrated the feasibility of creosote recovery from used wood ties with minimum decomposition of the wood matrix via a thermal desorption process. Our study was carried out at various temperatures using analytical thermochemical analysers such as thermogravimetric spectrometry (TGA) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The objective of this study was to investigate the recovery yield and composition of creosote desorbed from used wood ties under various thermal treatment conditions using a lab-scale fixed bed reactor with condensers. This study aim at quantifying creosote compounds as well as the decomposition of wood matrix during the various thermal treatment conditions. This study also addresses specific challenges associated with thermally treated wood ties as a quality feedstock for thermochemical processes such as pyrolysis, co-generation, or gasification.

2. Material and methods

2.1 Material

A used creosote-treated railroad tie was obtained from National Salvage & Services Corporation (Bloomington, IN, USA). The tie was ground into less than 2 mm particle sizes with a knife mill and further sieved to obtain a fraction with particle sizes between 0.45 – 2 mm. This latter fraction was used for all experiments.

2.2. Experimental set up and procedure

The thermal treatment experiment was carried out in a bench-scale fixed-bed reactor equipped with a condensation system (Fig. 1). The reactor was made of a 1.2 kW vertical furnace (MTI corp.) with a 300 mm long heating zone and a cylindrical quartz tube (internal diameter 47 mm, length 610 mm) with a sample holder consisting of porous stainless steel basket (pore size 0.37 mm, diameter 32 mm, length 250 mm) into which the sample was loaded. For each run, 30 g wood tie sample were loaded into the porous holder, inserted into the bottom of the quartz tube, away from the heated zone. A constant nitrogen purge gas at a flow rate of 4 L/min was maintained. The furnace was then heated to desired temperature (250, 275, 300, 325, or 350 °C) at a heating rate of 10 °C/min. Once the furnace reached the desired temperature, the sample holder was lifted up into the isothermal zone of the quartz tube in the furnace, where the wood tie sample was thermally treated for a 30 min residence time. After 30 min, the sample holder was lowered to the bottom of the quartz tube for cooling under continuous nitrogen flow. The vapors produced during the thermal desorption were transferred by the purge gas from the reactor into a series of liquid nitrogen-cooled condensers. The condensation section was comprised of four dewar-type glass condensers, which were filled up with liquid nitrogen to cool

down the condensers (Fig. 1). Species that condensed on the wall of the condensers were recovered and fractionated as discussed in the next section.

2.3. Characterization

2.3.1. Liquid fraction

Vapors condensed on the walls of the glass condensers were recovered either with 250 mL methanol (Fraction #1) or 250 mL dichloromethane (CH_2Cl_2) and followed by 250 mL of deionized water (Fraction #2). Fraction #1 was used to determine the water content and to identify condensable species using gas chromatography/mass spectrometry (GC/MS) while Fraction #2 was used to quantify the amount of creosote and wood-derived components. Each experiment was conducted in triplicate.

2.3.1.1. Characterization of liquid fraction #1

Water content in the liquid fraction #1 (methanol fraction) was measured by Karl Fischer titration (Metrohm 787 KF Titrino) according to the American Society for Testing and Materials (ASTM D4377). The chemical composition of this fraction was determined by GC/MS (Perkin Elmer Clarus 680 Gas Chromatograph coupled with a Clarus SQ 8C Mass Spectrometer). A 1.0 μL aliquot of solution was injected into the GC with the injection port maintained at 270 °C. The compounds were then separated using an Elite 1701 capillary column (60 m x 0.25 mm ID x 0.25 μm film thickness) with the following temperature program: 5 min at 50 °C, 5 °C min^{-1} to 280 °C and 20 min at 280 °C. Ultra-high pure helium was used as the carrier gas (1mL/min). The separated compounds were analyzed using a mass spectrometer (MS) with a source temperature of 270 °C and electron ionization of 70. Approximately 74 compounds with a peak to noise

height ratio $\geq 10:1$ were identified by comparison with the NIST mass spectra data library of fragmentation patterns.

2.3.1.2. Characterization of liquid fraction #2

The liquid fraction #2 (dichloromethane-water fraction) was further fractionated into four groups (PAHs, phenolics, light organics and anhydrosugars) that correspond to creosote and wood-derived compounds. The fractionation scheme is based on creosote extraction [12] and bio-oil fractionation [13, 14] methods and is outlined in Fig. 2. In this method, 500 mL of fraction #2 was placed in a 1000 mL separatory funnel and adjusted to pH 14 with sodium hydroxide (NaOH). All samples were extracted three times using dichloromethane (DCM), resulting in the transfer of non-polar creosote compounds including PAHs to the organic phase. The quantity of PAH compounds in the organic phase was determined gravimetrically after evaporating DCM using a rotary evaporator (IKA) and vacuum-drying at 40 °C. The aqueous phase, which contains lignin- and sugar-derived compounds from the wood matrix, was adjusted to pH 2 with hydrochloric acid (HCl) and extracted with DCM three times resulting in the transfer of lignin-derived phenolics in the organic phase. The aqueous phase was further extracted with diethyl ether to transfer light organics in the ether-soluble fraction and anhydrosugars in the ether-insoluble fraction. The light organics, anhydrosugars and phenolic fractions were further vacuum-dried at 40 °C and weighed.

2.3.2. Solid fraction

Water content in the solid fraction before and after thermal treatment was measured by the Karl Fischer titration method using a 2: 1(v/v %) mixture of methanol: chloroform with a titrant of hydranal composite 5K solution [15]. A thermogravimetric analyzer (Pyris 1 TGA, PerkinElmer) was used to evaluate the thermally treated wood ties with the temperature increasing from 30 to

800 °C at 10 °C/min and holding for 10 min at 800 °C under 20 mL/min of nitrogen gas flow. Proximate analysis including moisture content, ash content, volatile matter, and fixed carbon of the raw and thermally treated wood ties was determined 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). The higher heating value (HHV) of each thermally treated sample was calculated using an ordinary least-squares regression method [16]. Energy retained (HHV retained, %), defined as the amount of energy conserved in the solid part after the thermal treatment, was calculated by equations 1 and 2 [17]:

$$M_{retained} (\%) = 100 \times \frac{m_t}{m_i} \quad (\text{eq. 1})$$

$$HHV_{retained} (\%) = M_{retained} \times \frac{HHV_t}{HHV_i} \quad (\text{eq. 2})$$

where, $M_{retained}$ = mass retained after thermal treatment in percentage (%); m_t = mass of thermally treated sample; m_i = mass of raw sample; HHV_t = HHV of thermally treated sample; HHV_i = HHV of raw sample.

PAHs in the solid fraction of the raw and thermally treated wood ties were extracted with DCM using an accelerated solvent extractor (ASE 350, Dionex Corp.) at 100 °C and 9 cycles [18]. Extracted solvent (180 mL) was placed in a 1000 mL separatory funnel and subjected to fractionated scheme outlined in Fig.2. All thermal treatments were performed in triplicate.

3. Results and discussion

3.1. Thermal treatment

3.1.1. Mass loss

Used creosote wood tie samples were thermally treated at 250, 275, 300, 325, and 350 °C for a 30 min to desorb the creosote using a fixed bed reactor illustrated in Fig. 1. The mass loss

of the sample after thermal treatment was 13 wt% at 250 °C. As temperature increased, the mass loss increased to 20 wt% at 275 °C, 36 wt% at 300 °C, 50 wt% at 325 °C, and 63 wt% at 350 °C (Fig. 3). The mass loss in this study was comparable to the data obtained with a thermogravimetric analyser (TGA) in our previous study [11] demonstrating that the experimental setup of the lab-scale reactor was suitable for thermal treatment of the wood tie samples. It also suggests that thermal desorption of creosote-treated wood ties is scalable. The moisture content in the untreated and treated ties was measured by two techniques: Karl Fischer titration (KFT) and ASTM methods. As shown in Table 1, the moisture content determined by the ASTM method was always higher when compared to the KFT method. This observation suggests that an elevating temperature, as it is done in the ASTM moisture content method, results in gradual desorption of creosote thus leading to overestimating the moisture content of the ties.

3.1.2. Thermogravimetric analysis

The thermogravimetric profiles demonstrated the level of desorption of creosote and decomposition of wood matrix of the raw and thermally treated samples (Fig. 4). The TG thermograms (Fig. 4a) of the untreated sample exhibited a gradual increase of mass loss in the T1 and T2 regions followed by a drastic increase in T3 region and then a slow increase to 800 °C. The corresponding derivative of the thermograms (DTG) curve (Fig. 4b) of the untreated sample showed a small peak from the gradual mass loss in the T1 region associated with water removal and desorption of creosote. This observation is consistent with moisture content results shown in Table 1 and indicates that moisture content of creosote-treated ties is more accurately measured by Karl Fischer titration than the conventional oven drying technique due to desorption of creosote during the analysis. The broad peak in the T2 region was predominately associated with

mass loss by thermal desorption of creosote compounds with broad boiling points from 180 to 496 °C for the untreated sample. Finally, the major peaks in the T3 region represent the decomposition of cellulose, hemicellulose, and lignin in the wood matrix [19].

In contrast, the thermograms (Fig. 4a) of the thermally treated samples showed no change in mass in T1 and T2 regions but a drastic increase of mass loss at temperature ranging from 250 to 390 °C (T3 region) with a shift in initial degradation severity as treatment temperature increased. The DTG curves of treated ties at 250 °C exhibited a maxima peak at 370 °C with a shoulder peak at 318 °C in the T3 region. Interestingly, this shoulder peak at 318 °C was observed to be smaller than that of the untreated sample, suggesting that creosote compounds were also desorbed in this temperature region. As the wood ties were thermally treated from 250 to 300 °C, the shoulder peak at 318 °C gradually decreased and disappeared for the 300 °C-treated sample. The disappearance of the shoulder peak is associated with degradation of cellulose as well as hemicellulose in the wood matrix. The treated samples above 300 °C exhibited a reduction of the maxima peak at 370 °C indicative of a significant decomposition of cellulose.

3.2. Liquid products

3.2.1. Creosote recovery

Creosote compounds and wood-decomposed products in the liquid fraction collected from the condensers were analyzed using GC/MS before and after solvent fractionation. In total, 44 creosote compounds were identified by GC/MS (Table 2 and Supporting information Fig. A1). These creosote compounds have a broad spectrum of molecular weights (MW) ranging from 128 to 252 g/mol, boiling points from 218 to 495 °C, and vapor pressures from 12.3 to 10^{-6} Pa at 25 °C (Supporting Information Table A1). The recovered creosote contained mostly polycyclic

aromatic hydrocarbon (PAHs) compounds such as acenaphthylene, dibenzofuran, fluorene, phenanthrene, anthracene, benzo[def]fluorene, fluoranthene, pyrene, chrysene, and benz[a]anthracene and other PAHs, indicating that creosote compounds recovered from used wood ties were distilled from coal tar [20].

Upon thermal treatment at 250 °C, 47 % (5.1 of 11.1 wt%) of total PAHs present in the wood tie samples were recovered as illustrated in Fig. 5a. The samples treated at 275 and 300 °C desorbed 65 % (7.2 of 11.1 wt%) and 79 % (8.8 of 11.1 wt%) of PAHs, respectively. The recovery fractions of PAHs were 89 % (9.9 of 11.1 wt%) at 325 °C and 97 % (10.7 of 11.1 wt%) at 350 °C. Over 80 % of PAHs present in the used railroad ties were desorbed at temperature above 300 °C. In order to determine the distribution of PAH compounds recovered from the liquid fraction at different thermal treatment conditions, PAH compounds were categorized into eight groups based on their vapor pressures (*v.p.* Pa at 25 °C). For example; G1 ranged between 8.3 and 12.3 Pa, G2 between 1.7 – 2.5 Pa, G3 at 10^{-1} Pa, G4 at 10^{-2} Pa, G5 at 10^{-3} Pa, G6 at 10^{-4} Pa, G7 at 10^{-5} Pa, and G8 at 10^{-6} Pa (Fig. 5b and Supporting information Table A1). The classification was based on vapor pressures due to the fact that the volatilization of PAHs from treated wood in service depends on temperature and vapor pressure. In particular, vapor pressure is strongly positively correlated with the desorption rates of PAHs [21]. The GC/MS peak area distribution percentage of PAHs with broad vapor pressures (Fig. 5b) showed that the 250 °C-treated sample released more PAHs with lower molecular weights and higher vapor pressures. As temperature increased, so did the amount of PAHs with higher molecular weight and lower vapor pressures (Fig. 5b). The recovery of PAHs from the 250 °C-treated wood tie had the highest proportion (72 %) of PAHs with high vapor pressures, ranging between 10^{-3} - 12.3 Pa. These PAHs were mostly naphthalene, methyl naphthalene, dimethyl naphthalene,

methylbiophenyl, dibenzofuran, biophenyl, acenaphthylene, methyldibenzofuran, phenyl naphthalene, fluorene, methyl phenanthrene, benzo[def]fluorene, and fluoranthene (Fig. 5c - 5j). As temperature increased, the recovery of PAHs with higher vapor pressures diminished, whereas that of PAHs with higher molecular weight and lower vapor pressures ranging between 10^{-6} and 10^{-4} Pa (Fig. 5b), like anthracene, carbazole, pyrene, chrysene, 2,3-benzo[c]fluorene, benzo[a]anthracene, benzo[k]fluoranthene, benzo[l]fluoranthene, and benzo[a]pyrene gradually increased (Fig. 5c – 5j). In particular, PAHs such as benzo[a]pyrene and benzo[c]pyrene with a boiling point of 495 °C and vapor pressure of 1.6×10^{-6} Pa at 25 °C were observed at thermal treatment above 300 °C albeit in small quantities. PAH compounds recovered from the thermally treated wood ties at temperature above 300 °C had a similar distribution of PAHs present in the untreated sample although traceable PAHs with vapor pressures ranging between 10^{-5} and 10^{-6} Pa still remained in the thermally treated wood ties. The distribution of individual PAH compounds recovered from the untreated and thermally treated wood ties at above 300 °C was compared to those of fresh PAHs in AWWA (American Wood Preservers' Association) standard creosotes derived from coal tar [20], AWWA creosote contains a significantly higher proportion of PAHs with lower molecular weights and higher vapor pressures (10^{-3} – 12.3 Pa) including naphthalene, methylnaphthalene, biophenyl, acenaphthylene, phenanthrene, and fluorene than our recovered PAHs. This indicates that PAH compounds evaporate or leach, or that physicochemical and biological degradative processes selectively degrade PAHs with lower molecular weights and higher vapor pressures during the service life of ties [22]. It could also reflect a change in creosote formulation from the original creosote/coal tar blends or creosote/oil blends. In any event, it is believed that recovered creosote could be amended with a slight addition of oil or creosote components if needed before being reused.

3.2.2. Decomposition of wood matrix

The wood-decomposed products in the liquid fraction were analyzed using GC/MS after a solvent fractionation (Table 2 and Supporting information Fig. A1). Thermal treatment at 250 °C produced very small amounts of light organics, anhydrosugars, and phenolic compounds (Fig. A1) with acetic acid (**2**), levoglucosan (**43**), and several phenolic compounds (Fig. A1. and Table 2). The decomposition of the wood matrix started at temperature above 275 °C producing high peak intensity of light oxygenated compounds, glycolaldehyde (**1**), acetic acid (**2**), hydroxyacetone (**3**) and low peak intensity of furans, furfural (**10**), 2(5H)-furanone (**16**), levoglucosan (**43**), and phenolic compounds such as o-guaiacol (**19**), 4-vinylguaiacol (**25**), isoeugenol (**32**), 4-methoxy-3-(methoxyethyl)phenol (**33**), methoxyeugenol (**41**) with a slightly elevated amount of anhydrosugars and phenolic compounds. Acetic acid derived mostly from fragmented acetyl groups on pentosans in hemicellulose and from cellulose fragmentation reaction. These results demonstrated the drastic decomposition of hemicellulose and cellulose in the wood matrix at 275 °C, which was confirmed by the significant reduction of the shoulder peak in the DTG curve (Fig. 4b.) Other light organics (glycolaldehyde and hydroxyacetone) are also products of hemicellulose and cellulose fragmentation reactions. Furanic compounds (furfural and 2(5H)-furanone) are known to be products of carbohydrate (cellulose and hemicellulose) dehydration. Anhydrosugar (levoglucosan) is a product from depolymerisation of cellulose [23] while phenolic compounds are derived from lignin. These results indicate that hemicellulose, cellulose, and lignin gradually decomposed with temperature; for example, hemicellulose breaks down in the temperature ranging between 220 and 315 °C, cellulose between 240 and 360 °C, and lignin between 240 and 360 °C [24]. Thermal treatment at 300 °C increased the amount of anhydrosugars and phenolic compounds (Fig. 6), with the presence of

additional light organics (acetoxycetic acid (**6**), methyl pyruvate (**8**)), anhydrosugars (1,4:3,6-Dianhydro- α -D-glucopyranose (**24**)), and various phenolic compounds. Thermal treatment at 325 and 350 °C produced a large amount of anhydrosugars such as levoglucosan and 1,4:3,6-Dianhydro- α -D-glucopyranose (dehydrated from levoglucosan) demonstrating that the drastic reduction of DTG maximum peak at 370 °C was associated with cellulose (Fig. 4b). Reaction water was calculated by first determining the total mass of water in the liquid fraction using Karl Fischer titration followed by subtracting the mass of water that contributed from moisture in the creosote-treated wood tie sample (Fig. 6). The yield of reaction water increased with temperature from 250 to 300 °C and reached a plateau of around 23 - 25 wt% at temperatures between 300 – 350 °C, demonstrating a dramatic increase of reaction water yield at 300 °C at the expense of the decomposition of cellulose and hemicellulose by dehydration reaction [25, 26]. The products containing light organics, levoglucosan and monomeric phenolic compounds dissolved in the aqueous phase could be directly used as a potential substrate for an integrated pyrolysis-microbial electrolysis for hydrogen production or as intermediates to produce value-added chemicals [27].

3.3. Solid products

3.3.1. Creosote residue in the thermally treated wood

The amount of PAHs remaining in the thermally treated wood tie samples showed that the 250 °C-treated sample still contained 45 % (5.0 of 11.1 wt%) of the total PAHs (Fig. 7a). As temperature increased, 29 % of total PAHs remained in the 275 °C-treated wood tie and decreased to 13 % of PAHs in the 300 °C-treated wood tie. The thermally treated wood tie

sample at above 300 °C still contained very small amount of PAHs such as 8 % in the 325 °C-treated wood tie and 3 % in the 350 °C-treated wood tie.

The distribution of the PAH compounds with different vapor pressures showed that as temperature increased from 250 to 350 °C, the thermally treated samples had a higher proportion of the PAH compounds with lower MWs and higher vapor pressures ranging between 10^{-4} and 12.3 Pa and a lower proportion of the PAHs with higher MWs and lower vapor pressures ranging between 10^{-5} and 10^{-6} Pa (Fig. 7b - 7f). For example, samples treated with elevated temperature had a decreasing proportion of the PAHs with relatively higher vapor pressures ranging between 10^{-4} and 12.3 Pa such as acenaphthalene, phenanthrene, fluoranthene, anthracene, pyrene, methyl pyrene and chrysene and an increasing portion of the PAHs with relatively **lower** vapor pressures ranging between 10^{-5} and 10^{-6} Pa such as benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[l]fluoranthene, benzo[a]pyrene, and benzo[e]pyrene.

3.3.2. Solid matrix characterization

Wood tie samples thermally treated at different temperatures were characterized using proximate and ultimate analyses. The proximate analysis revealed the property changes in volatile matter (VM), fixed carbon (FC), and ash after thermal treatment. The VM content of creosote-treated sample was 86 wt%, while its FC content was 14 wt% (Table 1). As creosote-treated wood samples were thermally treated from 250 to 350 °C, VM decreased from 79 to 40 wt%, whereas FC increased from 17 to 52 wt%, demonstrating a linear decrease of VM with increasing FC (Table 1 and Fig. 8a). The main elements in creosote-treated wood sample include carbon (C), hydrogen (H), oxygen (O), and to a lesser extent nitrogen (N), which are important sources of heat in combustion. As the samples were thermally treated up to 350 °C, carbon content increased from 46.6 to 65.0 %, while hydrogen and oxygen decreased from **5.7** to 3.8 %, and

from 46.0 to 23.6 wt%, respectively (Table 1). It is worth noting that lower amount of oxygen and moisture produced with an elevated thermal treatment enhances the calorific value of the thermally treated tie wood. The atom oxygen-to-carbon (O/C) and hydrogen-to carbon (H/C) ratios in the non-thermally treated sample was 0.7 (O/C) and 1.5 (H/C), respectively (Fig. 8b). After thermal treatment at 250 °C, oxygen and hydrogen drastically decreased, indicative of a reduction of water produced mainly from the dehydration of the hydroxyls in cellulose and hemicellulose and evaporation of PAH compounds [28]. The van Krevelene diagram for the thermally treated wood from 250 to 350 °C followed a linear relationship with the atomic H/C ratio and the atomic O/C ratio (Fig. 8b), demonstrating the desorption of creosote compounds and decomposition of wood matrix. The higher heating value (HHV) of the non-thermally treated wood was approximately 17 MJ/kg (Fig. 8c). The thermal treatment from 250 to 350 °C induced an increase of HHVs from 19 to 23 MJ/kg, which is closer to the HHV (25 – 35 MJ/kg) of coal [29]. The energy retained (the total energy ratio between thermally treated wood and non-thermally treated wood) showed a gradual reduction from 93 to 87 % at temperatures from 250 to 275 °C and a more drastic reduction from 75 to 49 % at temperatures above 300 °C even though HHV is enhanced (Fig. 8c).

3.4. Applications

Based on the aforementioned results, it is important to consider temperature conditions regarding the trade-off between creosote recovery and upgradability of thermally treated wood tie material for market demands in subsequent thermochemical processes such as pyrolysis, co-generation, or gasification. One consideration to determine is the operational heating temperature needed to recover PAHs remaining in the used railroad ties. The PAHs recovery % from used railroad ties

exhibits a drastic linear increase to 65 % with a drop of solid yield to 80 wt% at a temperature of 275 °C, whereas a gradual linear increase of PAHs recovery from 79 to 97 % with a drastic decrease of solid yield from 64 to 37 wt% at temperature from 300 to 350 °C (Fig. 3). In addition, heating temperatures between 250 and 275 °C cause negligible hemicellulose degradation (Fig. 4), whereas heating temperatures above 300 °C show a drastic linear increase in yield of wood-derived components with degradation of hemicellulose, cellulose and lignin (Fig. 9). It is believed that temperatures ranging between 250 and 275 °C can recover a high purity of PAHs fraction with relatively low vapor pressures and molecular weights albeit with lower PAH recovery. At temperatures above 300 °C, it is possible to recover most PAH compounds in the wood. However, at such high temperatures significant quantities of carbohydrate and lignin-derived compounds will be mixed with the recovered PAHs, which could require further separation. Another consideration is the optimum operational temperature for the improvement of the thermally treated wood for downstream processing. Thermally treated tie-derived wood could be a potential source suitable for thermochemical conversion. Our study demonstrated that thermally treated tie-derived wood can avoid many limitations associated with the non-thermally treated wood, in a way similar to a torrefaction process [29], containing high carbon content, low O/C ratio, enhanced caloric values (19 – 23 MJ/kg), as well as low hazardous creosote residues. In particular, thermal treatment at 275 °C and 300 °C caused the energy retained in the wood to drop from 87 to 75 % and the HHV to increase between 19.6 and 20.4 MJ/kg (Fig. 9). This may be enough for tie-derived wood to provide a quality biomass for subsequent thermochemical processes such as pyrolysis, gasification and co-generation. For example, there would be a reduction in fossil fuel derived carbon dioxide (as the creosote would be re-used and not be burned), and the thermally treated wood ties could be a high quality feedstock for pyrolysis in a

similar way to torrefied biomass treated at 200 - 300 °C in an inert atmosphere. **Torrefaction improves a quality of biomass associated with grindability, hydrophobicity and energy density, making it more favorable for further processes such as combustion, gasification, and pyrolysis [30]. Furthermore, pyrolysis of torrefied biomass produces a high quality of bio-oil with low water content, acidity, and high pyrolytic lignin compounds as an intermediate source for a downstream refinery process [31].** Conversely, temperatures above 300 °C cause an energy retained to drop to 60 and 49 % but with PAH recovery up to 97%. This means that a larger amount of thermally treated wood would be required to produce the same unit of energy if used in thermochemical processes. Although this could be undesirable in terms of economics, the high value of the creosote should be more than enough to counter it. Taking into consideration the aforementioned factors involving PAH recovery, solid yield, energy yield, HHV as well as the energy costs associated with an elevated temperature and a subsequent thermochemical process, heating temperatures between 275 and 300 °C appear to be optimal.

4. Conclusions

Thermal desorption of preservative-treated wood is a good alternative technology for the re-use of used wood railroad ties. Our study demonstrates that thermal treatment ranging between 275 and 300 °C would be optimum to recover preservative to treat new wood tie products in order to offset the cost of the thermal treatment process, and to upgrade the wood quality for use as a feedstock for thermochemical processes such as pyrolysis and gasification to produce chemicals and renewable energy. It could also reduce negative environmental impacts including continuous release of hazardous air pollutants into the environment and emission of greenhouse gases if used wood ties are disposed of in landfills (both the replacement of the fuel with fossil fuel and the

release of methane). Future work will be conducted to scale up and commercially evaluate a thermal process of used railroad ties and utility poles focussing on both, an auger and fluidized bed reactor system.

Acknowledgements

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

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Fig. 1. Schematic representation of the laboratory scale thermal desorption reactor system. 1. Nitrogen gas cylinder, 2. Thermocouple measuring biomass bed temperature, 3. Furnace PID controller, 4. Tubular furnace, 5. Quartz tube reactor with porous stainless steel biomass sample holder, 6. Dewar like condensers filled with liquid nitrogen, 7. Liquid sample collection and 8. Outlet gas port

Fig. 2. Solvent fractionation scheme of PAHs and bio-oils. DCM stands for dichloromethane, NaOH for sodium hydroxide and HCl for hydrochloric acid.

Fig 3. Effect of temperature on mass loss of creosote treated wood tie samples with a 30 min residence time.

Fig. 4. Thermogravimetric curves of the raw and thermally treated wood tie samples at 250, 275, 300, 325, or 350 °C for 30 min residence time. (a) TG thermograms and (b) Derivative TG curves. T1, T2 and T3 represent temperature regions of 30 to 110 °C, 110 to 235 °C and 235 to 400 °C, respectively.

Fig. 5. Yield and GC peak area distribution % of PAH compounds recovered from the raw and thermally treated wood tie samples at 250, 275, 300, 325, or 350 $^{\circ}$ C. (a) Yield of PAH compounds and (b) GC peak area distribution % of PAHs with various vapor pressures, and (c) – (j) distribution of PAH compounds with various vapor pressures.

Fig. 6. Fractionation of products in liquid fraction decomposed from creosote-treated wood ties into reaction water, anhydrosugars, phenolics, light organics and furans.

Fig. 7. PAHs residues in the thermally treated wood tie samples. (a) PAHs residue (%) in solid and (b - f) distribution (peak area %) of PAHs compounds with various vapor pressures remaining in the thermally treated wood tie samples.

Fig. 8. Proximate and ultimate analysis of the wood tie sample treated at 250, 275, 300, 325, or 350 C. (a) Proximate analysis, (b) Van-Krevelen diagram, and (c) Higher heating value (HHV) and energy retained.

Fig. 9. Correlations between products from different thermal treatments. (a) PAHs recovery vs mass loss of wood tie, (b) PAHs recovery vs wood component in liquid fraction, and (c) PAH s recovery vs energy retained (%).

Table 1. Proximate and ultimate analysis of the raw and thermally treated wood tie samples at temperature ranging from 250 to 350 °C.

Sample	Moisture (wt % dry basis)		Proximate analysis (wt % dry basis)			Ultimate analysis (wt % dry basis)			
	KFT ¹	ASTM ²	VM	Ash	FC ³	C	H	N	O
Raw	6.5 (0.1)	8.1 (0.3)	85.5 (0.6)	1.4 (0.1)	13.7 (0.6)	46.6 (0.7)	5.7 (0.2)	0.2 (0.0)	46.0 (0.9)
250 °C	2.9 (0.2)	3.6 (0.2)	79.4 (0.7)	3.7 (0.7)	16.9 (0.7)	50.2 (0.2)	5.3 (0.1)	0.1 (0.1)	40.4 (0.3)
275 °C	2.2 (0.3)	3.0 (0.4)	75.2 (0.8)	3.9 (0.1)	20.8 (0.8)	51.6 (0.7)	5.3 (0.1)	0.2 (0.0)	39.0 (0.7)
300 °C	3.0 (0.2)	3.3 (0.4)	68.8 (0.8)	3.6 (0.1)	27.5 (0.7)	54.9 (0.3)	5.1 (0.2)	0.2 (0.1)	35.3 (0.3)
325 °C	2.2 (0.2)	2.5 (0.4)	52.8 (1.1)	7.0 (0.3)	40.5 (1.2)	60.2 (0.2)	4.4 (0.1)	0.3 (0.0)	28.1 (0.3)
350 °C	3.2 (0.2)	3.5 (0.3)	40.3 (0.4)	7.3 (0.1)	52.5 (0.4)	65.0 (0.3)	3.8 (0.1)	0.3 (0.0)	23.6 (0.4)

VM, FC, C, H, N and O stand for volatile matter, fixed carbon, carbon, hydrogen, nitrogen and oxygen.

¹⁾ Moisture content was determined by Karl Fischer titration.

²⁾ moisture was determined according to the ASTM standard.

³⁾ fixed carbon and was determined by difference.

⁴⁾ Oxygen content was determined by difference.

Numbers in the parentheses represent standard deviations.

Table 2. Organic compounds identified in the liquid fraction produced from raw and thermally treated tie samples.

No.	RT (min)	Compounds	Group	No.	RT (min)	Compounds	Group
1	6.6	Glycolaldehyde	^{a)} Ald	38	34.5	4-Methyldibenzofuran	Fur
2	7.4	Acetic acid	Acid	39	34.9	3,5-Dimethoxyacetophenone	PAH
3	8.4	Hydroxyacetone	^{a)} Ket	40	35.0	4-Methyldibenzofuran	PAH
4	10.3	Propanoic acid	Acid	41	35.3	Methoxyeugenol	Lig
5	11.2	1-Hydroxy-2-butanone	Ket	42	36.5	9-Methylfluorene	PAH
6	11.3	Acetoxyacetic acid	Acid	43	37.6	Levogluconan	AnS
7	12.0	Dimethoxytetrahydrofuran	^{a)} Fur	44	37.8	Methoxyeugenol	Lig
8	12.7	Methyl pyruvate	^{a)} Est	45	38.3	Dibenzothiophene	PAH
9	13.1	Dimethoxytetrahydrofuran	Fur	46	39.0	Phenanthrene	PAH
10	13.3	Furfural	Fur	47	39.1	Anthracene	PAH
11	14.9	Acetol acetate	Est	48	40.7	Desaspidinol	Lig
12	15.5	(2-Hydroxy-1-methoxy)ethylfuran	Fur	49	41.1	1-Methylphenanthrene	PAH
13	17.0	2-Hydroxy-2-cyclopenten-1-one	Ket	50	41.2	2-Methylphenanthrene	PAH
14	17.7	5-Methylfurfural	Fur	51	41.6	Benzo[def]fluorine	PAH
15	17.9	1-Acetoxy-2-butanone	Ket	52	41.8	3-Methylphenanthrene	PAH
16	18.7	2(5H)-Furanone	Fur	53	42.4	2-Phenylnaphthalene	PAH
17	19.6	1,1-Dimethoxyhexane	^{a)} Lig	54	42.6	Carbazole	PAH
18	20.1	3-Methyl-1,2-cyclopentanedione		55	43.6	Anthraquinone	PAH
19	21.5	o-Guaiacol	Lig	56	44.8	Fluoranthene	PAH
20	23.2	Naphthalene	^{b)} PAH	57	45.6	Benzonaphthofuran	PAH
21	24.4	Homoguaiacol	Lig	58	45.8	Pyrene	PAH
22	26.2	1-Methylnaphthalene	PAH	59	46.9	2-Methylfluoranthene	PAH
23	26.7	2-Methylnaphthalene	PAH	60	47.3	Benzo[c]fluorine	PAH
24	27.7	1,4:3,6-Dianhydro- α -d-glucopyranose	^{a)} AnS	61	47.6	2,3-Benzofluorene	PAH
25	28.2	4-Vinylguaiacol	Lig	62	47.8	1-Methylpyrene	PAH
26	28.4	Biphenyl	PAH	63	50.4	3,4-Benzo-9-thiafluorene	PAH
27	29.5	1,7-Dimethylnaphthalene	PAH	64	50.5	Benzo[c]phenanthrene	PAH
28	29.6	2,6-Dimethylnaphthalene	PAH	65	50.8	Benzo[ghi]fluoranthene	PAH
29	30.1	1,4-Dimethylnaphthalene	PAH	66	51.8	Chrysene	PAH
30	31.0	4-Methylbiphenyl	PAH	67	52.0	Benz[a]anthracene	PAH
31	31.4	Acenaphthylene	PAH	68	52.2	3,4-Benzophenanthrene	PAH
32	31.5	Isoeugenol	Lig	69	55.3	Benzo[a]carbazole	PAH
33	31.8	4-Methoxy-3-(methoxymethyl)phenol	Lig	70	59.7	Benzo[b]fluoranthene	PAH
34	32.4	Dibenzofuran	PAH	71	59.9	Benzo[k]fluoranthene	PAH
35	33.6	5-tert-Butylpyrogallol	Lig	72	62.2	Benzo[l]fluoranthene	PAH
36	34.0	Fluorene	PAH	73	62.7	Benzo[a]pyrene	PAH
37	34.1	1-Allylnaphthalene	PAH	74	63.8	4,5-Benzopyrene	PAH

^{a)} Ald stands for aldehyde, Est for ester, Ket for ketone, Fur for furan, Lig for lignin, AnS for anhydrosugars. ^{b)} PAH represents polycyclic aromatic hydrocarbons (PAHs).