Thermal desorption of creosote remaining in used railroad ties: Investigation by TGA (thermogravimetric analysis) and Py-GC/MS (pyrolysis-gas chromatography/mass spectrometry)

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ARTICLE INFO

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 10–30 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.

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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 PAHs (polycyclic aromatic hydrocarbons), is a probable human carcinogen [3]. Approximately 9 kg of creosote is impregnated in about 0.1 m^3 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 NHSM (Non Hazardous Secondary Materials) 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 TWC (Treated Wood Council), 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

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

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 5 K 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].

$$Mp = \frac{Mt}{Mo} \times 100 \ (\%) \tag{1}$$

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

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 PerkinElmer 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, 1 mL/min) that passes through the furnace. The vapor was then separated using an Elite 1701 MS capillary column (60 m × 0.25 mm ID × 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.