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Recovery of creosote from used railroad ties by thermal desorption

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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 and 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.

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/m^3 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

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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 and 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

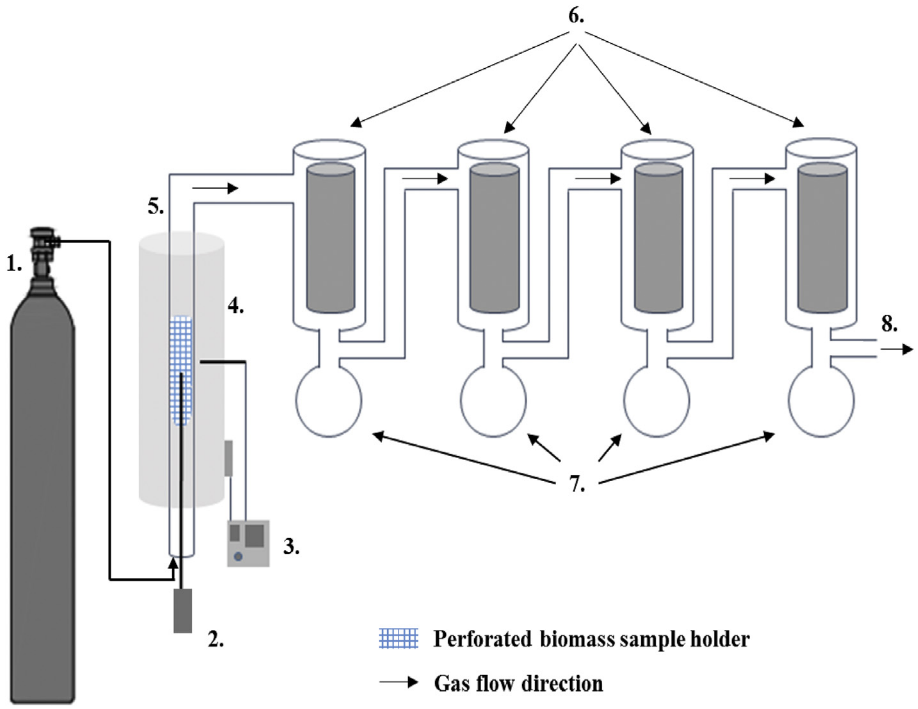

Fig. 1. Schematic representation of the laboratory scale thermal desorption reactor system. **1**. Nitrogen gas cylinder, **2**. Thermocouple measuring biomass bed temperature, **3**. Furnace PID controller, **4**. Tubular furnace, **5**. Quartz tube reactor with porous stainless steel biomass sample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