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Research article

# The effects of weathering on the pyrolysis of low-carbon fuels: Railway ties and asphalt shingles

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ABSTRACT

Creosote-treated wooden railway ties and roofing asphalt shingles are discarded in large quantities and may be significant sources of energy; however, they may have rotted or oxidized, and the chemical changes that result from such weathering could affect their behavior as a fuel or pyrolysis feedstock. Such changes in railway tie wood, and roofing asphalt shingles were studied by identifying isothermal 250 and 550 °C pyrolysis products (pyrolyzates) with pyrolysis-gas chromatography/mass spectrometry (py-GC/MS). Poplar wood pyrolysis was also studied and compared to existing literature to establish a reference scenario; identified poplar wood pyrolyzates assisted in the analysis of railway tie and asphalt shingle pyrolyzates. Poplar pyrolyzates included the products of polysaccharide ring-breaking and lignin pyrolysis, confirming one of the two competing low-temperature pyrolysis models. Railway tie pyrolyzates showed few signs of bacterial degradation or oxidation, indicating that the tie considered here did not undergo extensive weathering. Roofing asphalt pyrolyzates included many carbonyl, hydroxyl, and ether functionalized cyclic species, as well as sulfur dioxide; these pyrolyzates indicate extensive and preferential oxidation of cyclic carbon and sulfur.

## 1. Introduction

### 1.1. Background

Low carbon fuels (LCFs) include solid end-of-life materials, wastes and virgin and non-virgin biomass that are used as fossil fuel alternatives because they have lower life-cycle carbon emissions than traditional fossil fuels, such as coal. When LCFs are considered for use, their combustion behavior must be considered. The combustion and pyrolysis behavior of a fuel will be dependent on its chemical makeup. Due to the uses of many end-of-life LCFs, they may have undergone significant weathering (i.e. oxidation or microbial digestion), which may have changed their chemistry compared to their initial product state.

Of particular interest here are the large quantities of creosote-treated wooden railway ties and roofing asphalt shingles that are discarded annually [1,2]. Discarded railway ties are typically 35 years old [1], whereas the age of waste shingles ranges from 12 to 20 years [2]. These materials are possible fuels or pyrolysis feedstocks and as such the effect of weathering on their chemistry must be explored. Pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) has been applied to determine the chemical structure of many fuels, as well as fuel pyrolysis behavior, by identifying and quantifying pyrolysis products or “pyrolyzates” [3]. Py-GC/MS has been applied extensively to wood [4], and should be a useful tool to explore the chemical changes that have occurred in railway tie wood or roofing asphalt shingles.

#### 1.1.1. Railway ties

Wood railway ties are infused with creosote, which ensures an operational life of 25–30 years [5]. A railway tie's chemical makeup is therefore dependent on both the wood and its creosote content; a tie is typically 85% wood and 15% creosote, by weight.

Wood is primarily composed of three bio-polymers: two polysaccharides, cellulose and hemicellulose, and a phenolic polymer, lignin [6]. All three polymers rot or oxidize — for instance, the carbonyl content of lignin increases during oxidation or microbial digestion [7]. Creosote is a coal tar distillate with antibacterial and antifungal properties, and is predominantly composed of aromatic and polycyclic aromatic hydrocarbons (PAHs) [8]. Creosote does not affect wood chemistry, except in that it preserves the wood and may prevent chemical changes; however, rotting and oxidation depend on environmental factors, and creosote does not completely halt microbial activity [9]. It is therefore difficult to predict the extent of rot or oxidation that may have occurred before the disposal of a railway tie. A study by Cooper et al. [10] on utility poles found that the only evidence of decay in creosote-treated poles was shallow surface soft rot either at or below the groundline portions of the older (older than 25 years) poles. However, the study noted that poles older than 20 years have levels of creosote that are either approaching or are below toxic thresholds for decay fungi, and therefore decay may occur. Unlike utility poles that are placed into the ground,

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railway ties sit on two layers of ballast: top ballast and sub-ballast. The top ballast allows drainage, while the sub-ballast prevents subgrade soil from penetrating the top ballast [5]. This environment is therefore less likely to encourage rotting.

During pyrolysis, wood polysaccharides produce pyranic and furanic compounds, while lignin produces phenolic species. These pyrolyzates indicate polymer structure [11–14]. Coal derived creosotes contain approximately 85% aromatic hydrocarbons. Therefore the creosote pyrolyzates mainly consist of polycyclic aromatic hydrocarbons [14]. Railway tie pyrolyzates may show to what extent its wood chemistry has changed due to oxidation or rotting.

### 1.1.2. Asphalt shingles

Pyrolyzates may also indicate to what extent roofing asphalt shingles have oxidized, particularly the asphalt fraction. Asphalt is produced from the residuum of petroleum fractionation, or harvested from bitumen. Asphalt chemistry is complex and is dependent on its source and how it was processed; however, the gross chemical structure of asphalt is well understood. Asphalt is a homogenous, impermeable, colloidal substance composed of solids (asphaltenes) distributed in an oily matrix (maltenes) [15]. Asphaltenes are large molecules, composed of cyclic cores connected by aliphatic bridges. Maltenes are smaller and may be divided into saturated, aromatic and resinous fractions. Asphalt may be oxidized during production, and may also oxidize under exposure to light and air; oxidized asphalt contains sulfone, carbonyl and hydroxy functions [16,17]. During pyrolysis, asphaltenes tend to produce cyclic and linear pyrolyzates (from cyclic or aliphatic structures [18–20]), whereas maltenes tend to evaporate [19]. Therefore, oxygenated pyrolyzates may be associated with specific asphalt structures and thereby show the extent and pathway of asphalt oxidation.

### 1.1.3. Poplar

Poplar wood would be useful as a reference py-GC/MS material when identifying railway tie and asphalt pyrolyzates. Identified poplar pyrolyzates can be compared with published results; poplar pyrolyzates are therefore easy to identify. Comparisons between the mass and retention times of poplar pyrolyzates and those produced by railway ties and asphalt thus helps confirm their identity. As discussed above, wood is composed of cellulose, hemicellulose and lignin, each of which pyrolyze differently. Wood pyrolysis therefore produces a complex mixture of different species, many of which are commercially valuable as fuels or raw materials [21]. Wood pyrolysis is therefore a subject of interest, and poplar pyrolysis has been particularly well-studied [11,21–23]. However, the mechanism of wood pyrolysis — specifically, of the cellulose fraction — is disputed. Diebold [24] proposed that cellulose pyrolysis proceeded by competing dehydration, chain cleavage, vapourization and char-formation reactions, see Fig. 1. According to that model, low-temperature cellulose pyrolysis produces char, water, a small amount of carbon dioxide and a smaller amount of oxygenated, gaseous hydrocarbons. However, Gu et al. [25] observed that 250–350 °C poplar pyrolysis produced more carbon dioxide than water, which is inconsistent with Diebold's model. Gao et al. [26] observed similar $CO_2$ emissions during low-temperature pine pyrolysis. In response to these findings, Gu et al. proposed that cellulose and hemicellulose pyrolysis proceeded by depolymerization and pyranose ring-breaking; products of these reactions may further degrade to oxygenated hydrocarbons, or repolymerize into char, see Fig. 2.

Low-temperature pyrolysis has been studied with hyphenated thermogravimetric techniques, particularly thermogravimetric-mass spectrometry (TG-MS) and thermogravimetric-fourier transform infrared spectroscopy (TG-FTIR). These techniques can only identify permanent gases or small hydrocarbons, as they do not separate pyrolyzates [27]; for instance, the largest pine pyrolyzate identified by Gao et al. (using TG-FTIR) was phenol ($M = 94$ u) [26]. Py-GC/MS is capable of identifying a much larger number of pyrolyzates, by separating pyrolyzates in the gas chromatograph. Py-GC/MS has been used to study high-temperature pyrolysis ($T > 350$ °C); however, as pyrolysis has a slow rate of reaction at low temperatures, it has been difficult to study low-temperature pyrolysis with py-GC/MS [11]. Increasing sample mass or pyrolysis time may increase the rate of eluted gases sufficiently to identify those pyrolyzates, which may confirm, or refute, the proposed pyrolysis mechanism of Gu et al.

## 1.2. Objective of study

The objective of this study was to identify as many as possible 250 and 550 °C pyrolysis products of discarded creosote-treated wooden railway ties, and discarded asphalt shingles, in order to determine the effects of weathering on their chemistry.

## 1.3. Scope of study

The objective of the study was accomplished by completing the following tasks:

1. Identify pyrolysis products of poplar at 550 °C to validate the method and approach.
2. Perform poplar pyrolysis at 250 °C to determine whether results are more consistent with pyrolysis mechanisms proposed by either Gu, et al. or Diebold.
3. Perform 250 and 550 °C pyrolysis on a discarded railway tie and a discarded asphalt shingle samples to determine the effects of weathering after their disposal and subsequent use as a fuel.

# 2. Experimental approach

## 2.1. Materials

A discarded creosote-treated wooden railway tie, which was at least 20 years old, was obtained from near Gananoque, Ontario. Poplar (*Populus hybrid*) was harvested from a greenhouse near Cornwall,

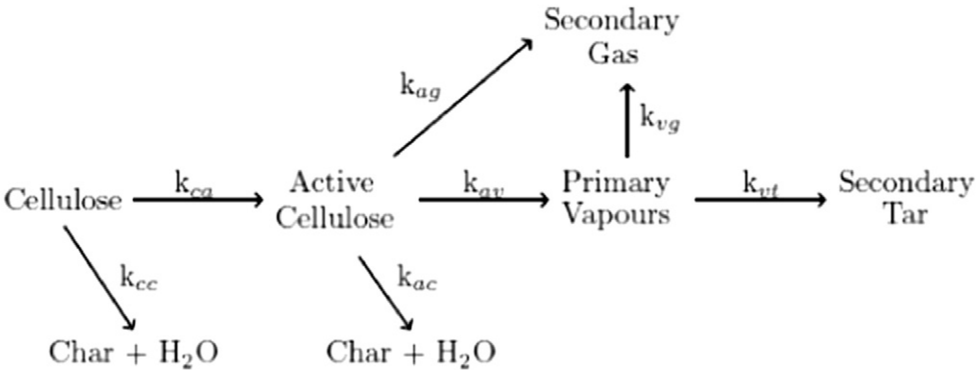

**Fig. 1.** Diebold's [24] proposed cellulose pyrolysis mechanism.