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Evaluation of the antioxidant activities of different bio-oils and their phenolic distilled fractions for wood preservation

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ABSTRACT

This research investigated the antioxidant activities of raw bio-oils produced from pine and oak wood species. The study also included the effect of the pyrolysis parameters on the properties of the bio-oils produced. In addition to raw bio-oils, phenolic fractions were further isolated from the bio-oils at two different temperature ranges (180–220 °C and 220–270 °C) by using spinning band distillation columns. The antioxidant activities of raw bio-oils and phenolic fractions were evaluated using the Trolox equivalent antioxidant capacity (TEAC) assay. The concentrations of phenolic compounds were determined by gas chromatography/mass spectrometry (GC/MS). The results of the assay showed that the antioxidant activities of the phenolic fractions are much higher than those of the parent bio-oils. GC/MS analysis results showed that *o*-guaiacol and its derivatives (4-methylguaiacol, 4-ethylguaiacol, and 4-propylguiacol), phenol, 3-methylphenol, 2,3-dimethylphenols, 3-ethylphenol, and eugenol are the most influential phenolic compounds on the antioxidant activity of the bio-oils and their distilled fractions.

1. Introduction

Wood is one of the most important materials available to human beings. It is inexpensive, renewable, and has unique properties compared with other materials that make it highly beneficial for residential, commercial, and industrial use. However, wood may be readily damaged and destroyed by a variety of biodegrading organisms and microbes such as fungi and bacteria, termites, insects, and marine borers because of its organic chemical structure (Sundararaj et al., 2015). In general, wood degrading processes can cause billions of dollars loss every year to repair and replace the damaged wood structures (Goodell et al., 2003). Accordingly, treatment of wood with chemical preservatives to prevent its damage by these aggressive biodeteriogens is very important. The treatment has a dual advantage of extending the service life of the wooden material and conserving the forest resources (Schultz et al., 2007).

Traditionally, oil-borne organic solvent preservatives (creosote and penta) and the water-borne chromated copper arsenate (CCA) were the major three 1st-generation wood preservatives for many decades due to their long term effectiveness, low cost, and robust formulations that were easy to use in a treating facility (Schultz and Nicholas, 2008). In the last thirty years, health and environmental concerns associated with CCA, penta, and creosote arose rapidly all over the world and pressed for the development of 2nd-generation copper- rich preservatives. However, the growing environmental concerns about disposal of toxic copper leaching chemicals directed wood preservation industry toward more environmentally benign alternatives that are effective and cheap as traditional wood preservatives (Ahn et al., 2008). The current state of art wood preservatives emphasis on using totally organic compounds and non-biocidal systems (3rd and 4th-generation) to protect wood (Schultz and Nicholas, 2008).

Termites and fungi are the two extremely harmful forces which can destroy any wood species. Wood decay fungi is of interest because without fungi wood would never decay, the two major decay fungi are brown-rot and white-rot fungi. Brown-rot fungi are the most destructive type of decay fungi especially for wood components in service (Cheng et al., 2008). This type of fungi attacks only the cellulose components of the cell wall in softwoods. On the other hand, white-rot fungi prefer hardwoods and attack both the lignin and cellulose components of the cell wall. The most acceptable mechanism for brown-rot decay is the production of

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hydroxyl radical ($OH^{\bullet}$) via the Fenton reaction or one-electron oxidation (Enoki et al., 1997; Highley and Flournoy, 1994). The $OH^{\bullet}$ radical are the tool that fungi use for non-enzymatic attack to break though the walls of the wood cells (Schultz et al., 2005). It was also proposed that decay fungi use metal ions native to wood such as iron(II) or copper(I) for this reaction (Jensen et al., 2001):

$$Fe^{2+}\left(Cu^{+}\right) + H_2O_2 + H^{+} \rightarrow Fe^{3+}\left(Cu^{2+}\right) + H_2O + OH^{\cdot} \quad (1)$$

Therefore, any compound that is capable of neutralizing the $OH^{\bullet}$ radicals and/or chelating the metal ions, would be able to prevent this non-enzymatic radical attack, and may be useful as wood preservative against fungal decay (Binbuga et al., 2005). Focus in the current study was given to scavenging the free radicals and not to the metal chelation. It has been shown that effective radical-scavenging compounds are polyphenolic organic species, such as tannins and flavonoids (Boligon et al., 2009; Obanda et al., 2008). These compounds are able to rapidly neutralize free radicals, leaving stable unreactive products (Aadil et al., 2014), and therefore may be useful as wood preservatives and fungal inhibitors. In the current study, a particular attention will be given to the phenolic compounds.

The last two decades have witnessed an increased interest in using renewable biomass feedstocks as a source for energy and chemical feedstocks. Bio-oil, a product of the pyrolysis of biomass, is considered to be an excellent source for environmentally benign, totally organic, polyphenolic compounds (Temiz et al., 2013) that are able to neutralize the free radicals. Bio-oils also add structural integrity to wood, have a pleasing appearance when applied, non-hazardous, and not only abundant in nature, but easily replenished and sustained (No, 2014). Bio-oils are also cheaply produced; the cost to produce bio−oils is $0.62−1.40/gal or $0.16−0.35/liter (Shemfe et al., 2015). Antifungal properties of several pyrolytic bio-oils and their lignin-rich fractions were tested previously and showed excellent decay protection in soil block tests (Mohan et al., 2008). In a recent study, bio-oil obtained from the fast pyrolysis poplar wood showed good decay resistance against wood-rot fungi. The phenolic compounds derived from lignin played an important role against fungal attack (Yen and Chang, 2008). Antifungal activity of liquefied wood and liquefied wood containing biocide were also tested against the selected wood degrading fungi in several studies (Hrastnik et al., 2013; Humar et al., 2011).

Determining major phenolic compounds in the bio-oil and their lignin-rich fraction that potentially have higher antioxidant activity is important. Identification of these chemicals will help to use them directly as antifungal agents for wood preservation. To the best of our knowledge, there are no previous studies on the identification of the major phenolic compounds that potentially have high antioxidant activity in the bio-oil. Therefore, the main objectives of this research were to measure the antioxidant activities for raw bio-oils and their phenolic distilled fractions and determine the phenolic compounds that greatly affect the antioxidant capacity.

2. Materials and methods

2.1. Materials

In the current study, twenty four bio-oils were used, eight of them were obtained from the National Renewable Energy Laboratory (NREL) (Golden, CO) and sixteen were prepared at Mississippi State University (MSU) using an auger reactor.

2.2. Bio-oil preparation

The NREL bio-oils were prepared from oak and pine woods in a fixed-bed reactor. The preparation conditions and parameters (the type of wood species, temperature, and residence time) are summarized in Table 1. The MSU bio-oils were produced through the pyrolysis of oak wood, pine wood, oak bark, and pine bark in the auger reactor. The oak and pine wood feedstocks were supplied by Fiber Resources, Inc. (Pine Bluff, AR) in the form of wood pellets. The pine bark and oak bark were supplied by Packaging

Table 1
Description of the different bio-oils used in this study.

Bio-oil (ID)	Bio-oil description	Bio-oil source
BO-1	Oak wood, low temperature, long residence time	NREL
BO-2	Oak wood, high temperature, long residence time	NREL
BO-3	Oak bark, low temperature, long residence time	MSU
BO-4	Oak bark, low temperature, short residence time	MSU
BO-5	Oak bark, high temperature, long residence time	MSU
BO-6	Oak bark, high temperature, short residence time	MSU
BO-7	Oak wood, low temperature, long residence time	MSU
BO-8	Oak wood, low temperature, short residence time	MSU
BO-9	Oak wood, high temperature, long residence time	MSU
BO-10	Oak wood, high temperature, short residence time	MSU
BO-11	Pine bark, low temperature, long residence time	MSU
BO-12	Pine bark, low temperature, short residence time	MSU
BO-13	Pine bark, high temperature, long residence time	MSU
BO-14	Pine bark, high temperature, short residence time	MSU
BO-15	Pine wood, low temperature, long residence time	MSU
BO-16	Pine wood, low temperature, short residence time	MSU
BO-17	Pine wood, high temperature, long residence time	MSU
BO-18	Pine wood, high temperature, short residence time	MSU
BO-19	Pine wood, high temperature, long residence time	NREL
BO-20	Pine wood, low temperature, short residence time	NREL
BO-21	Pine wood, high temperature, short residence time	NREL
BO-22	Pine wood, low temperature, long residence time	NREL
BO-23	Oak wood, low temperature, short residence time	NREL
BO-24	Oak wood, high temperature, short residence time	NREL

High temperature = 550 °C for NREL bio-oil and 450 °C for MSU bio-oil.
Low temperature = 500 °C for NREL bio-oil and 400 °C for MSU bio-oil.
Short residence time = 4 s for both NREL and MSU bio-oil.
Long residence time = 6 s for both NREL and MSU bio-oil.