



Research Paper

Potential antioxidants for biodiesel from a softwood lignin pyrolyzate



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ABSTRACT

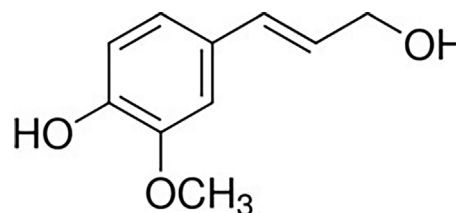
Softwood lignin was pyrolyzed to afford a “bio-oil” distillate in which phenols were major products. Extraction with alkali gave a range of lignin-related phenols having molecular weights (MWs) from 110 to 344 amu. The total phenolic extract was at least equal in antioxidant activity to the synthetic compound 2,6-di(*tert*)butyl-4-methylphenol (BHT). The extract was separated by chromatographic techniques to characterize components potentially responsible for the activity. A series of phenols in the extract exhibited MWs of 274, 302, 316, 330, and 344 and are likely to be dimers responsible for the majority of the observed antioxidant properties. Several of these compounds appear by mass spectrometry to be bifunctional phenolic compounds containing catechol or guaiacol groups. We hypothesize that a type of effective antioxidant for fatty acid esters will contain one phenolic hydroxyl group hydrogen-bonded to the ester and another at a radical-quenching site; monophenols are likely to be ineffective in this system due to the predominance of hydrogen bonding (kinetic solvent effect).

1. Introduction

Antioxidant compounds are valuable additives used to slow or prevent oxidative degradation of useful materials. Although many commercial antioxidants are petroleum-derived synthetic compounds, there has been an increasing interest in use of renewable or naturally occurring substances.

Mixtures of pyrolysis products from plant materials have been shown to contain active antioxidants (Nsimba et al., 2012; Ma et al., 2013). Antioxidant activity has often been measured by means of quenching experiments using stable free radicals in polar environments. Because radical quenching kinetics are highly dependent on solvent polarity (Howard and Ingold, 1964), these products should also be tested in less polar materials such as vinyl polymers, hydrocarbon fuels, and lipid-based products such as biodiesels (fatty acid methyl esters).

Pyrolysis of wood gives rise to products largely derived by thermal degradation of its principal constituents cellulose and hemicellulose, which are carbohydrate polymers, and lignin, a polyphenol. Lignins vary among plant types: those of softwoods (e.g., pine, spruce) are mainly derived from the oxidative polymerization of the C₆–C₃ derivative, coniferyl alcohol (Structure 1).

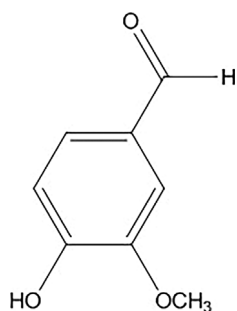


Coniferyl alcohol

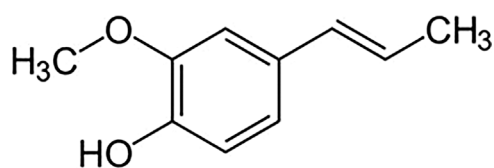
A typical pyrolysis study of lignins (Saiz-Jimenez and de Leeuw, 1984) showed that spruce lignin contained many phenolic compounds derived from guaiacyl residues, including guaiacol (2-methoxyphenol), 4-methylguaiacol, carbonyl compounds such as vanillin (Structure 2), and phenols with extended conjugation such as isoeugenol (Structure 3).

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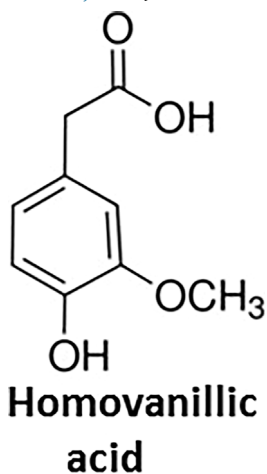


Vanillin



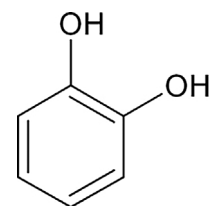
Isoeugenol

Kraft lignin (a product of pine), in addition, had homovanillic acid (Structure 4) as a major product. Higher molecular weight phenols (dimers and oligomers) related to lignin are also formed under a wide range of heating conditions, ranging from seconds (Patwardhan et al., 2011) to days (Guillen and Ibargoitia, 1999). These oligomers may result from secondary thermal reactions of monomeric phenols in the vapor phase (Patwardhan et al., 2011).



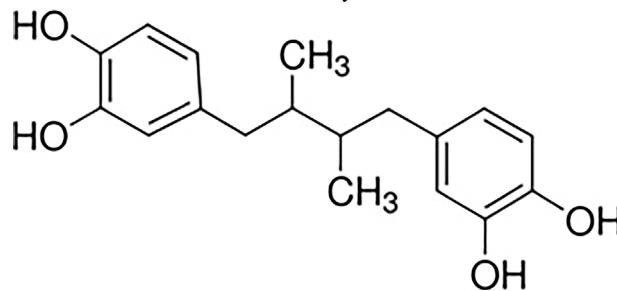
Homovanillic acid

Phenolic compounds derived from lignin decomposition have been shown in a variety of environments to be more or less effective antioxidants. Many of these studies have examined the performance of individual phenols in simple radical-quenching measurements, such as electron spin resonance, bleaching of crocin, diphenylpicrylhydrazyl (DPPH) radical scavenging, and inhibited peroxidation of styrene (Uchida et al., 1996; Barclay et al., 1997; Ogata et al., 1997; Bortolomeazzi et al., 2006). In general, these experiments show that phenols with extended conjugation or dihydroxyphenols such as catechol (Structure 5) are also occasionally noted as highly active compounds (Botella et al., 2014).



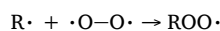
Catechol

Naturally occurring phenolic dimers have frequently been demonstrated to be superior to monomeric antioxidants in a variety of systems. To give only a few examples, N-coumaryl- and N-feruloyltyramine from *Lycium barbarum* were potent antioxidants (superior to BHA) in DPPH and lipid peroxidation assays (Gao et al., 2015; Forino et al., 2016); dimeric flavolignans similarly scavenged DPPH more readily than their monomeric analogues (Gavezzotti et al., 2014); and a dimer of ferulic acid from rye was better than its monomer in the inhibition of copper-catalyzed lipoprotein oxidation (Andreasen et al., 2001). Nordihydroguaiaretic acid (NDGA, structure 6), a lignan from the creosote bush, is formally a dimer of 4-isopropenyl catechol. It was widely used as an antioxidant for dairy products in the 1950s and 1960s (Stull et al., 1948) but was banned due to its toxicity.

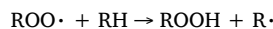


NDGA

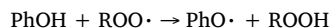
Biodiesel is quite susceptible to oxidative degradation due to its content of unsaturated fatty acid esters. The initial step of oxidation of these materials is the formation of peroxy radicals by the diffusion-controlled addition of molecular oxygen to a carbon-centered radical, $R\cdot$;



These radicals then go on to continue a “chain reaction” by abstracting a reactive H-atom from a donor, RH;



The chain-breaking inhibitor (PhOH, in the case of a phenol) acts by intercepting the peroxy radical and forming a new, less reactive radical that cannot continue the chain.



Commercially available antioxidants for biodiesel principally use hindered phenols such as BHT, but one product (Baynox +, Lanxess, Cologne, Germany) contains a dimer of BHT with two phenolic -OH groups, and another (Bioextend, Eastman, Kingsport, TN) features *t*-butylhydroquinone (TBHQ), which also has two such groups (Voegelé, 2011). Extracts derived from natural plant materials have been tested for their antioxidant activity in biodiesel (Medeiros et al., 2014; Spacino et al., 2016). Adding extracts of rosemary, oregano, and basil, which contain complex polyphenols and lignan dimers such as rosmarinic acid (Structure 7), to soy biodiesel greatly increased oxidative stability.

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