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Effect of sulfuric acid addition on the yield and composition of lignin derived oligomers obtained by the auger and fast pyrolysis of Douglas-fir wood

Shuai Zhou [a], Noridah B. Osman [b], Hui Li [b], Armando G. McDonald [b], Daniel Mourant [c], Chun-Zhu Li [c], Manuel Garcia-Perez [a,*]

[a] Biological Systems Engineering, Washington State University, Pullman, WA 99164, USA
[b] Renewable Materials Program, Department of Forest, Rangeland and Fire Science, University of Idaho, Moscow, ID 83844, USA
[c] Fuels and Energy Technology Institute, Curtin University, Perth, WA 6102, Australia

HIGHLIGHTS

- The use of sulfuric acid as additive in pyrolysis mitigates the undesirable catalytic effect of alkalines.
- The addition of sulfuric acid enhances the production of anhydrosugars but decreases the yield of lignin derived oligomers.
- Sulfuric acid affects mostly lignin derived oligomeric fractions with guaiacyl (G) units (with methoxyl groups).
- Sulfuric acid seems to catalyze the dehydration of 1,2-aryl migration intermediates and enhances the formation of char.

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ABSTRACT

This paper investigates the effect of sulfuric acid (H_2SO_4) concentration, as an additive to enhance the production of anhydrosugars via pyrolysis of Douglas-fir, on the yield and composition of the lignin derived oligomers. Pyrolysis tests at 500 °C were conducted in auger and fluidized bed reactors. For both reactors the yield of lignin derived oligomers decreased as H_2SO_4 was added. Several analytical techniques (UV-fluorescence, TGA, ESI-MS, FTIR, solid state ^{13}C NMR and Pyrolysis-GC/MS) were used to characterize the lignin derived oligomers collected. Four peaks were observed in the UV-fluorescence spectra. The addition of H_2SO_4 reduces the yield of all the peaks. DTG curves also show the presence of several peaks. The addition of H_2SO_4 decreased the yield of all the peaks but its effect was more pronounced on peaks at 320 and 400 °C. Electrospray ionization-mass spectrometry studies did not show any major change on the molecular weight of the lignin oligomers ionized products obtained as a function of H_2SO_4 concentration. Solid state NMR results indicate that the methoxyl groups decreased and the carbonyl increased gradually as sulfuric acid concentration increases. The Py-GC/MS confirmed the phenolic compounds with methoxyl substitutions were substantially reduced as the acid concentration increased. The experimental results obtained suggest the presence of H_2SO_4 enhances the polycondensation of methoxyl substituted aromatic rings.

1. Introduction

Distributed fast pyrolysis units located close to biomass resources could convert between 60 and 75 mass% of lignocellulosic materials into crude bio-oils [1] of which 40% could be further transformed into transportation fuels via hydrotreatment in rural or centralized bio-refineries [2,3]. This technology is especially well suited for the conversion of lignin [4,5]. One quarter of lignin is converted into monomers, one quarter into oligomers and half into char [4,5]. These lignin derived compounds have been extensively characterized [6–9]. The selectivity of lignin and cellulose reactions towards the production of precursors of transportation fuels (monomeric and oligomeric lignin products and anhydrosugars) is very sensitive to pyrolysis temperature, the presence of alkaline metals, and to the particle size used [4,5,10,11]. The conversion of cellulose to anhydrosugars (levoglucosan, cellobiosan), is currently limited to approximately 20%, the rest being transformed into other fractions with lower economic value (small molecules and char). The presence of alkalines, and the cellulose–lignin interactions are often cited as the main causes for the poor selectivity of cellulose thermochemical reactions towards the production of anhydrosugars.

* Corresponding author. Tel.: +1 509 335 7758; fax: +1 509 335 2722.
E-mail address: mgarcia-perez@wsu.edu (M. Garcia-Perez).

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Table 1
Yield of pyrolysis products as a function of H_2SO_4 concentration.

H_2SO_4 concentration (%)	Bio-oil yield (mass%)		Char yield (mass%)		Gas yield[a] (mass%)	
	Auger	Fluidized Bed	Auger	Fluidized Bed	Auger	Fluidized Bed
0	61.3 ± 3.9	55.6 ± 1.2	17.0 ± 1.3	12.2 ± 0.5	21.7 ± 5.0	32.2 ± 1.2
0.05	57.5 ± 1.9	62.6 ± 6.1	21.2 ± 3.5	12.2 ± 1.4	21.4 ± 2.8	25.2 ± 6.0
0.10	64.4 ± 1.2	51.8 ± 1.7	14.5 ± 1.0	19.9 ± 1.2	21.2 ± 2.2	28.4 ± 0.6
0.30	60.5 ± 2.5	49.2 ± 0.6	21.6 ± 1.1	22.8 ± 0.2	17.9 ± 3.5	28.0 ± 0.8
0.50	56.4 ± 1.9	47.1 ± 2.0	22.5 ± 1.7	25.6 ± 0.6	21.2 ± 3.3	27.3 ± 0.6

[a] The gas yield was calculated by difference.

Table 2
Effect of H_2SO_4 addition to Douglas-fir on the pyrolysis yield of lignin derived oligomers.

H_2SO_4 concentration (%)	Auger	Fluidized Bed
0	7.7 ± 0.9	11.4 ± 1.8
0.05	7.8 ± 1.3	8.7 ± 1.7
0.10	6.8 ± 0.7	5.8 ± 0.3
0.30	6.5 ± 0.5	5.4 ± 0.3
0.50	7.0 ± 2.1	5.1 ± 0.2

For more than 20 years, the thermo-chemical conversion community has been studying the use of additives to increase the yields of anhydrosugars [12–17]. Adding small amounts of H_2SO_4 to biomass is known to increase the yield of levoglucosan from some lignocellulosic materials [14,18]. Radlein et al. [15,16] explored the use of acid pre-treated wood to increase the production of sugars and proved that 80% of the pre-treated hollocellulose (cellulose + hemicelluloses) can be converted to sugars. Brown [13] found that the increase in the yield of sugars observed when small amounts of acids are added is due to the passivation of the catalytic effect of alkaline cations through the formation of stable salts. Brown [13] based his conclusions on a linear correlation obtained between the amount of minerals in the biomass and the amount of acids required to achieve maximum yields of levoglucosan. However, it is not known what the effect of adding a small

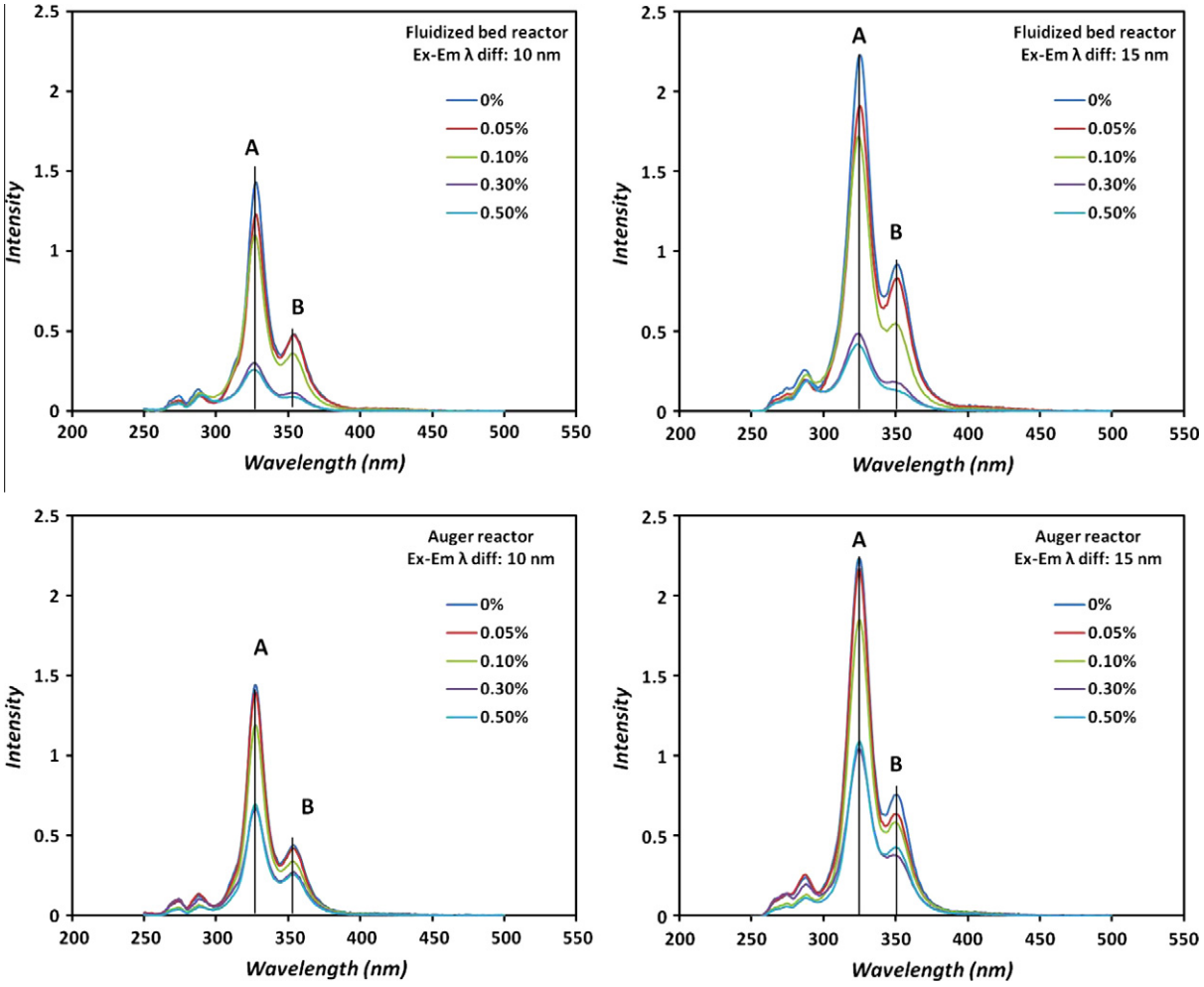

Fig. 1. UV-fluorescence spectra of lignin oligomers from fluidized bed and auger pyrolysis reactors (excitation wavelength: 250–500 nm, emission wavelength: 260–510 (difference 10 nm) and 265–515 (difference 15 nm).