

# Bio-renewable Precursor Fibers from Lignin/Poly lactide Blends for Conversion to Carbon Fibers

Mahendra Thunga<sup>1,2</sup>, Keke Chen<sup>1</sup>, Michael R. Kessler<sup>1,2,3,\*</sup>

<sup>1</sup>*Department of Materials Science and Engineering, Iowa State University, Ames, IA, USA.*

<sup>2</sup>*Ames Laboratory, US Dept. of Energy, Ames, IA, USA*

<sup>3</sup>*School of Mechanical and Materials Engineering, Washington State University, Pullman, WA,  
E-mail: [MichaelR.Kessler@wsu.edu](mailto:MichaelR.Kessler@wsu.edu)*

## Supporting information

### Experimental

#### *Lignin Modification*

Lignin was butyrated using the procedure described by W. Thielemans et al. [1]. Kraft softwood lignin and butyric anhydride were added into a two-necked flask at a weight ratio of 1:2 with 1 g of 1MIM catalyst for every 40 g of lignin. The reaction was carried out in nitrogen atmosphere under vigorous stirring at 50 °C for several hours to ensure complete conversion of the hydroxyl groups into ester groups. After the reaction was completed, ethyl ether was added at a 1:1 volume ratio and the mixture was then washed with deionized water to separate the catalyst 1MIM from the system. Cyclohexane was then added to the entire solution to sediment the lignin phase. The modified lignin (butyrated lignin, B-lignin) was vacuum-filtered and dried in a vacuum oven for 24 h and then ground into a fine powder before blending with PLA. The B-lignin was stored in a dry atmosphere and dried again at 60 °C for 12 h before melt processing. Complete butyration was confirmed by nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy

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with a Varian VXR-300 NMR spectrometer. Samples were prepared by dissolving unmodified lignin and B-lignin in DMSO-d<sub>6</sub>.

## Results and Discussion

### *Preparation and Properties of Modified Lignin*

A wide range of lignin modification methods have been developed to study the structure of lignin [2], and some were focused on the development of new materials and chemicals [3,4]. The chemical modification selected in this work facilitated improved miscibility between lignin and PLA by reducing the high polarity of lignin caused by its large number of hydroxyl groups.

Scheme S1 shows how lignin was passivized by esterification via butyration. The butyric anhydride reacted with 1-methylimidazole (1MIM) to form an N-alkyl-N'-methylimidazolium ion, which then reacted irreversibly with an alcohol group to form an ester group. R and R' may be any aliphatic or aromatic hydroxyl groups in the lignin. During butyration, the hydroxyl groups in lignin were expected to be replaced by ester groups, as shown in Scheme S2.

Before and after esterification, <sup>1</sup>H NMR spectroscopy was performed on lignin to study the nature of the ester bonds formed during modification. The <sup>1</sup>H NMR spectra shown in Figure S1a and 1b correspond to kraft lignin and butyrated kraft lignin, respectively. The chemical shift assessments listed in Table 1 compare literature [Error! Bookmark not defined.] values with the experimental values. Complete esterification of lignin was qualitatively confirmed by the signals appearing between 0.5 – 2.4 ppm and the simultaneous disappearance of the aromatic hydroxyl (ArOH) signal (8 – 10.5 ppm) in the NMR spectra of modified lignin (Figure S1a). The distinct signals between 0.5 – 2.4 ppm corresponded to the α-CH<sub>2</sub> (2.0 – 2.4 ppm), β-CH<sub>2</sub> (1.25 – 1.8 ppm), and –CH<sub>3</sub> (0.5 – 1.09 ppm) groups in the newly formed butyl ester group. During the butyration of lignin, all –OH groups were expected to be replaced by butyric ester chains.

However, in order to quantify the conversion of –OH groups to esters, it was necessary to measure the (ArOH) and the aliphatic hydroxyl (AlOH) groups separately. In fact, because of the interference of the signals in the  $^1\text{H}$  NMR spectra, it was difficult to measure the exact number of –OH groups. Literature data [**Error! Bookmark not defined.**] established that the peak corresponding to ArOH groups (8 – 10.5 ppm) in Figure S1a overlapped with the aldehyde (-CHO) groups, and the peak corresponding to AlOH groups (2.7 – 4 ppm) is from AlOH and methoxyl (-OCH<sub>3</sub>) groups. Therefore, the concentrations of the aldehyde (-CHO) and methoxyl (-OCH<sub>3</sub>) groups published in literature were subtracted from the areas under the corresponding peaks to measure the total number of –OH groups in pure lignin. The signal for aromatic photos (8 – 6.2) was used as a reference signal for measuring the degree of conversion of aromatic (ArOH) and aliphatic hydroxide (AlOH) groups to ester. The area under the characteristic peaks for -CH<sub>3</sub> bonds (0.5 – 1.09) in the butyric ester group was measured to estimate the number of ester chains present in lignin after modification. Table 1 shows that the total amount of ArOH and AlOH replaced by ester groups was equal to 1.01 PPU, which is approximately equal to the number of ester chains (1.159 PPU) as calculated from the –CH<sub>3</sub> bonds. Reducing these surface hydroxyl groups can significantly reduce the high polarity of lignin, so that lignin will completely dissolve in low polar organic solvents.

Table S1: Quantitative analysis of functional groups present in lignin

Functional groups	Softwood lignin <sup>a</sup>	Softwood lignin <sup>b</sup>	Butyrated softwood lignin <sup>b</sup>
Aromatic hydroxyl (ArOH)	0.64	0.634	0.012
Aliphatic hydroxyl (AlOH)	0.439	0.426	0.037
Carboxylic acid (-COOH)	0.11	NM	NM
Methoxyl (-OCH <sub>3</sub> )	0.76	NM	NM
Aromatic hydrogen (ArH) <sup>ref</sup>	2.5	2.5	2.5
Aldehyde (-CHO)	<0.02 <sup>a</sup>	<0.02 <sup>a</sup>	<0.02 <sup>a</sup>
-CH <sub>3</sub>	-	0.139	1.159

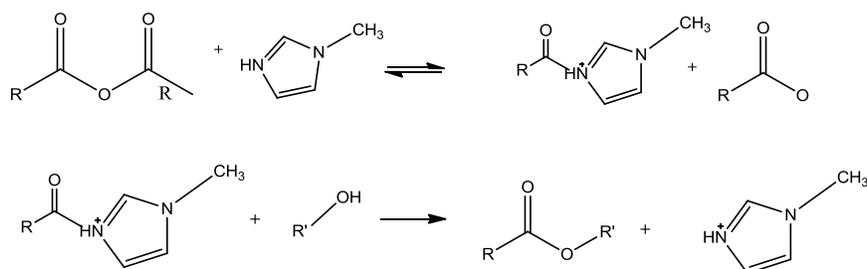
All values are in PPU

<sup>ref</sup> Reference signal

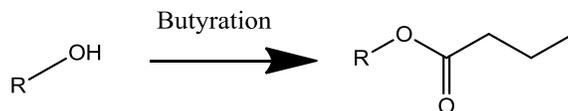
<sup>a</sup> Values according to [**Error! Bookmark not defined.**]

<sup>b</sup> Experimental values from the present <sup>1</sup>H NMR investigations

NM Not measured



Scheme S1. Reaction scheme of 1MIM catalyst esterification



Scheme S2. Conversion of hydroxyl groups to ester groups

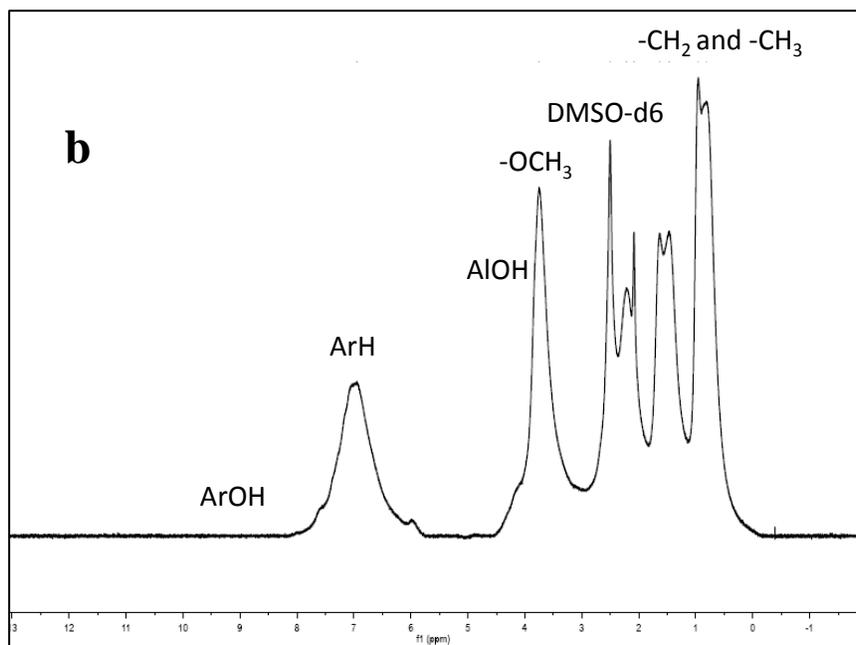
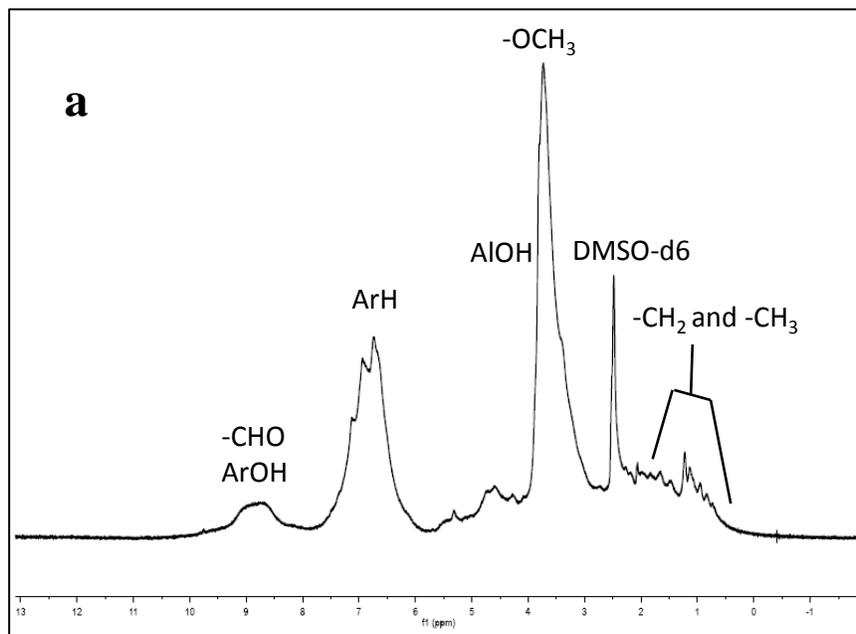


Figure S1.  $^1\text{H}$  NMR spectrum of softwood kraft lignin; (a) lignin before butyration; (b) after butyration

## Referances

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