Full Length Article

Oxidative degradation of the extraction residue from a sawdust

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GRAPHICAL ABSTRACT

Typical products from the oxidative degradation of the extraction residue (ER) and their possible precursors in the ER.
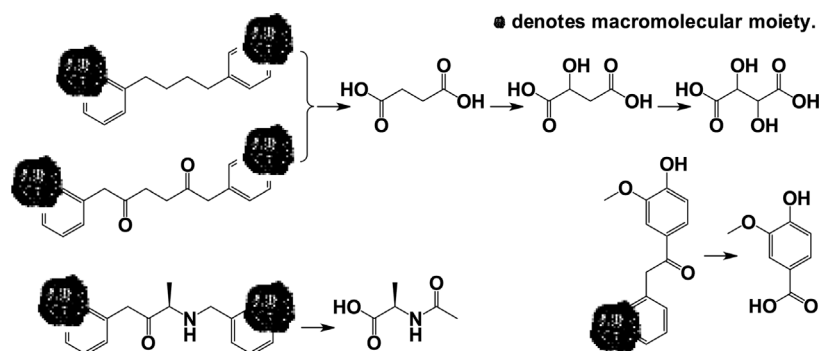
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ABSTRACT

The extraction residue (ER) from a sawdust was oxidatively degraded with aqueous hydrogen peroxide (AHPO)/ acetic anhydride (AAH) under mild conditions. About 16.1% of organic matter in the ER was converted to soluble portion (SP). In total, 76 compounds were detected in the SP from the reaction mixture by two-dimensional gas chromatography/time of flight-mass spectrometry. They can be classified into 20 group components. Among them, carboxylic acids (CAs) are the most abundant, accounting for ca. 57.2%. Most of the CAs are non-aromatic ones, especially non-aromatic dicarboxylic acids. All the esters produced from the ER degradation are acetates and diacetates. The results suggest that molecular composition of macromolecular species in the sawdust is complicated and the species without highly condensed aromatic rings tend to be oxidatively degraded to soluble compounds with AHPO/AAH. In addition, $CH_3COO^{\cdot}$ from AAH decomposition involved in the oxidative degradation of the sawdust.

1. Introduction

The existing utilization methods of biomass face difficulties in the harsh reaction conditions. Therefore, seeking for mild degradation methods to obtain value-added chemicals and liquid fuel is reasonable. Many oxidants, such as H_2O_2 [1], O_2/alkali [2,3], $RuCl_3$ [4–8], NaOCl [9,10], and aqueous hydrogen peroxide (AHPO)/acetic anhydride (AAH) [11,12], has been used for coal conversion under mild conditions. Among them AHPO/AAH is relatively cheap, ecofriendly, and strong as an oxidant. However, few reports are issued on the oxidative degradation (OD) of any biomass with AHPO/AAH.

Lignin is a class of important components in biomass and rich in

Nomenclature

AAAAs	acetamidoalkanoic acid
AAH	acetic anhydride
AAs	alkanoic acids
ACAs	aromatic carboxylic acids
ADAs	alkanedioic acids
ADs	alkane-1,2-diols
AHPO	aqueous hydrogen peroxide
ARs	aromatic rings
ATCAs	alkanetricarboxylic acids
BAs	branched alkanes
BCAs	benzenecarboxylic acids
CAs	carboxylic acids
C_β	carbon in β-position
CTDMGC/TOF-MS	comprehensive two-dimensional gas chromatograph/time of flight-mass spectrometer
DCAs	dicarboxylic acids
EE	ethoxyethane
ER	extraction residue from sawdust
ES	extract solution from the extraction of FC with EE
FC	filter cake from the reaction mixture of the ER with AHPO/AAH
FR	free radical
HAAs	hydroxyalkanic acids
HADAs	hydroxyalkanedioic acids
H, G & S	*p*-hydroxyphenylpropane, guaiacol, and syringol
HMBA	4-hydroxy-3-methoxybenzoic acid
MA	malic acid
MCAs	monocarboxylic acids
MEPs	methyl esterified products
MMSs	macromolecular species
NAs	normal alkanes
NARCAs	non-aromatic ring CAs
NARDCAs	non-aromatic ring DCAs
NCDCAs	nitrogen-containing DCAs
OAAs	oxoalanoic acids
OCs	other compounds
OD	oxidative degradation
ODCAs	other DCAs
OMCAs	other MCAs
R_{OD}	residue from oxidative degradation of the ER
RSD	relative standard deviation
SA	succinic acid
SP	soluble portion
TA	tartaric acid
TCAs	tricarboxylic acids

sawdust. *p*-Hydroxyphenylpropane, guaiacol, and syringol (H, G & S) are generally considered as main unit components forming macromolecular species (MMSs) in lignin [13]. The MMSs can be isolated by extracting small molecules [14] to avoid the disturbance of the small molecules for understanding the mechanisms for lignin degradation. Compared to common gas chromatograph/mass spectrometer, comprehensive two-dimensional gas chromatograph/time of flight-mass spectrometer (CTDMGC/TOF-MS) separates complex organic mixture and identifies the separated compounds much more effectively [15–22].

Taking the above considerations into account, we investigated OD of the extraction residue (ER) from a sawdust sample using AHPO/AAH as the oxidant and CTDMGC/TOF-MS to analyze the products from the ER degradation.

2. Experimental

2.1. Materials

The sawdust used was from Canadian hemlock and collected from a wood processing factory in Xuzhou, China. It was pulverized to pass through an 80-mesh sieve and dried in a vacuum at 80 °C for 24 h followed by sequential extraction with petroleum ether, carbon disulfide, methanol, acetone, isometric carbon disulfide/acetone, tetrahydrofuran, and isometric tetrahydrofuran/carbon disulfide mixed solvent under ultrasonication to afford the ER. Table 1 lists the proximate and ultimate analyses of the ER, which were determined by GB/T 212-2008 and Elementar Vario Macro. The proximate and ultimate

Table 1
Proximate and ultimate analyses (wt%) of the ER.

Proximate analysis			Ultimate analysis (daf)				$S_{t, d}$
M_{ad}	A_d	V_{daf}	C	H	N	O^a	
9.8	0.29	76.4	48.12	7.56	0.08	> 44.21	0.03

daf: dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base); V_{daf}: volatile matter (dry and ash-free base).
[a] By difference.

analyses are estimated to have 5% and 3% expanded uncertainties, respectively. AHPO (30%), AAH, CH_3CN, and ethoxyethane (EE) are commercially purchased analytical reagents from Xilong Chemical Co., Ltd, Guangdong, China, and distilled before use.

2.2. Experimental procedure

As displayed in Fig. 1, the ER (0.1 g), CH_3CN (50 mL), and AAH (10 mL) were added to a 250 mL three-necked spherical flask and fully mixed by magnetic agitation. Subsequently, AHPO (10 mL) was dropwise added into the mixture within 10 min using a drop funnel. Afterwards, the mixture was magnetically stirred at 55 °C for 24 h followed by filtration to afford a filtrate and filter cake (FC). By extraction with EE, the FC was separated to R_{OD} (residue from OD of the ER) and extractable solution (ES). The ES was incorporated into the filtrate and then evaporated under reduced pressure with a Büchi P-6 multivapor to afford the extract, which was esterified with diazomethane in EE at 35 °C for 8 h to afford methyl esterified portion (MEP). The resulting soluble portion (SP) yield was calculated on dried and ash-free (daf) basis of the ER. All the experiments were repeated at least 3 times to make the errors within ± 3%.

2.3. Analytical methods

The MEP was analyzed with a LECO Pegasus-IV CTDMGC/TOF-MS system equipped with 2 GC columns, i.e., a non-polar Rxi-5Sil MS (30 m × 0.25 mm ID × 0.25 μm film thickness) and a polar Rxi-17 (1 m × 0.1 mm ID × 0.1 μm film thickness). Helium was used as the carrier gas with a flow rate of 1 mL min^{-1} and split ratio of 20:1. The temperature program of the first column started at 60 °C for 0.5 min and then to 280 °C at 5 °C min^{-1}, and kept at 280 °C for 10 min. The second column was set at an offset value of + 5 °C from the first column heating program to compensate it. The modulator bias and modulation period are + 25 °C and 4 s, respectively. The m/z ranged from 35 to 500 and identification of compounds was realized by Chroma TOF v4.51.6.0 through comparing the acquired spectra with the NIST11 database. The yield (Y_i) of each compound analyzed were calculated according to the ratio of the compound mass (m_i) to the mass (m_{ER}) of organic matter in the ER, i.e., $Y_i = m_i/m_{ER}$. Each sample was analyzed with CTDMGC/