



Quenching of reactive intermediates during mechanochemical depolymerization of lignin

Alex D. Brittain^{a,b}, Natasha J. Chrisandina^a, Rachel E. Cooper^a, Michael Buchanan^b, John R. Cort^c, Mariefel V. Olarte^d, Carsten Sievers^{a,b,*}

^a Georgia Institute of Technology, School of Chemical & Biomolecular Engineering, Atlanta, GA 30332, United States

^b Georgia Institute of Technology, Renewable Bioproducts Institute, Atlanta, GA 30332, United States

^c Biological Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, United States

^d Chemical and Biological Processes Development Group, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, United States

ARTICLE INFO

Keywords:

Mechanocatalysis
Biomass
Ball mill
Organosolv lignin
Scavenger
Hydrolysis

ABSTRACT

Mechanochemical reactions are performed to depolymerize organosolv lignin with sodium hydroxide in a mixer ball mill. GPC analysis reveals that rapid depolymerization into small oligomers occurs within minutes of milling time, followed by a slower reduction in average relative molecular mass over the next 8 h of milling. Monomeric products are identified by GC-MS and quantified by GC-FID. The extent of depolymerization appears to be limited by repolymerization reactions that form bonds between products. Suppression of these repolymerization reactions can be achieved through the addition of methanol as a scavenger or adjustment of the moisture content of the feedstock. These modifications result in lower average relative molecular masses and higher yields of monomers. These results are an important step towards designing an efficient pathway for lignin valorization.

1. Introduction

Conversion of lignocellulosic biomass to biofuels and chemicals has attracted tremendous interest in recent years [1]. The U.S. Department of Agriculture and the Department of Energy have mandated that 20% of liquid transportation fuels and 25% of chemicals and materials should be derived from biomass by 2022, and this has driven research in the conversion of raw biomass into valuable products [2]. While many promising concepts have been developed for the conversion of cellulose and hemicellulose, the lignin fraction of lignocellulosic biomass remains underutilized [3]. In 2004, the pulp and paper industry alone produced 50 million tons of extracted lignin, but only 2% were used for commercial products rather than low-value fuel [4]. Therefore, the effective and efficient valorization of lignin has great potential for providing additional revenue [3,5].

Lignin does not have a regular, repeating structure like cellulose but consists of a three-dimensional amorphous polymer comprised of aromatic rings of varying functionalization, primarily hydroxyl, methoxy, and propyl groups [6]. The three most abundant monomeric species are typically guaiacyl, syringyl, and *p*-hydroxyphenyl units [1]. Due to the diversity of linkages between these monomeric units, lignin is more difficult to depolymerize than cellulose [7]. In addition, lignin exhibits poor solubility in many solvents, which creates particular

difficulty for heterogeneously catalyzed conversion [4]. Pre-treatment with ionic liquids [8] or ozone [9] increases the susceptibility of lignin to enzymatic hydrolysis. Steam explosion also cleaves β -O-4 bonds, which are the most abundant linkages in lignin [10]. Various basic catalysts have been used to depolymerize lignin in batch reactors, and sodium hydroxide has consistently emerged as an effective option [6,11]. Unfortunately, depolymerization under alkaline conditions generally results in the formation of large amounts of aqueous waste, high consumption of base, and presents problems for the isolation of products [4].

Another issue that often reduces the effectiveness of lignin depolymerization is that many lignin fragments can undergo condensation reactions [4]. Repolymerization can occur simultaneously with depolymerization, and reactive intermediates can react to form stable carbon-carbon linkages [10]. Such repolymerization reactions can be prevented with scavengers, notably phenol, alcohols like methanol and ethanol, or formaldehyde [11–15]. These scavengers convert reactive intermediates to stable molecules before these can cross-link with other lignin fragments.

Many processes for the conversion of lignocellulosic biomass require pre-treatment before the depolymerization reaction, which adds an extra step to the process [4,6,16]. Milling has been used in academia and industry to reduce the crystallinity of cellulose in biomass.

* Corresponding author at: Georgia Institute of Technology, School of Chemical & Biomolecular Engineering, Atlanta, GA 30332, United States.
E-mail address: carsten.sievers@chbe.gatech.edu (C. Sievers).

<http://dx.doi.org/10.1016/j.cattod.2017.04.066>

Received 21 December 2016; Received in revised form 7 April 2017; Accepted 30 April 2017
0920-5861/© 2017 Elsevier B.V. All rights reserved.

However, this pre-treatment often requires long milling times and only marginally reduces the molecular mass of biomass components. As an option for more direct depolymerization of biomass, mechanochemical depolymerization has gained attention [17]. Mechanochemistry uses mechanical energy provided by a ball mill to drive a solventless catalytic reaction at ambient conditions, avoiding issues caused by the poor solubility of biomass polymers (i.e. cellulose, lignin) in most common solvents. Mechanochemical ball milling has been used to produce water-soluble oligosaccharides from cellulose by hydrolysis with both solid acid catalysts and after impregnation with liquid acids [18–25] and to cleave β -O-4 bonds in lignin and model compounds with sodium hydroxide catalysts [26]. More limited cleavage of β -O-4 bonds in lignin model compounds was also observed through mechanochemical milling in the presence of water [27–32]. Various hypotheses for the way in which mechanochemistry operates have been proposed, including that friction provides energy in the form of high temperature pockets that enable molecules to overcome a solid–solid diffusion barrier [21,26,33–35], or that mechanical impact deforms molecules resulting in higher, more reactive energy states [34,36].

In mechanochemical conversion of cellulose, high yields of oligomers are readily obtained, but yields of monomeric products are relatively low [19]. Several theories for this phenomenon have been put forth [19,22]. Some attention has been paid to the moisture content of feedstock, because the dominant reaction is presumed to be hydrolysis [19,21]. While the addition of certain quantities of water is necessary to provide an otherwise limiting reactant [37], addition of excess water can result in a plasticization, which dissipates the mechanical energy from grinding, limiting chemical reactions or preventing grinding altogether in extreme cases [38]. Another theory for the limited depolymerization is the occurrence of repolymerization reactions [19,22], similar to the reactions of intermediates in thermochemical processes [19,39]. Thus, it will be important to explore ways for preventing repolymerization of reactive intermediates in mechanochemical reactions.

In this work, mechanochemical reactions for lignin depolymerization with sodium hydroxide are investigated. Prevention of repolymerization reactions through the use of methanol as a scavenger is also studied. Finally, the effects of the moisture content of the lignin feedstock are explored. Molecular weight analysis of the products is performed by GPC, monomeric products are identified and quantified by GC analysis, and an analysis of chain length distributions is obtained by LC-MS. In addition, linkage motifs of selected samples are examined by HSQC NMR.

2. Experimental section

2.1. Materials

Organosolv lignin from beech was obtained from Fraunhofer Institut in Leuna, Germany. Sodium hydroxide (ACS reagent, $\geq 97.0\%$, pellets), methanol (ACS spectrophotometric grade, $\geq 99.9\%$), methanol (CHROMASOLV[®] for HPLC, $\geq 99.9\%$), tetrahydrofuran (ACS reagent, $> 99.0\%$), acetic acid (glacial, ACS reagent, $\geq 99.7\%$), and 3,5 dimethoxyphenol (99%) were purchased from Sigma-Aldrich. Hydrochloric acid (ACS reagent, 36.5–38.0%, liquid) and o-xylene (99%) were obtained from Alfa Aesar. Ethyl acetate (ACS reagent, 99.9%) was purchased from Fisher Scientific. d_6 -DMSO was obtained from Cambridge Isotope Laboratories.

2.2. Moisture content of organosolv lignin sample

Five samples of the original organosolv lignin (2.00 g) were placed in an oven at 105 °C to evaporate the water content of the sample. The samples were weighed periodically to track changes in mass. After 48 h, when the samples had reached constant masses, the moisture content was calculated as the average of the five samples using the following

equation:

$$\text{Moisture Content (wt\%)} = \frac{m_{\text{totalsample}} - m_{\text{driedsample}}}{m_{\text{totalsample}}} * 100\% \quad (1)$$

2.3. Mechanochemical reactions

Ball-milling of lignin was performed in stainless steel vessels (25 mL) using a Retsch MM400 ball mill at room temperature. The vessels were equipped with three milling balls each (12 mm diameter, stainless steel). The ball-milling was carried out at 800 rpm (13.3 Hz) for 0–8 h. To avoid overheating at long milling times, the mill was stopped for 10 min after every 30 min of milling. For all tests, the milling vessel was filled with organosolv lignin (1.50 g) and sodium hydroxide pellets (1.50 g). For ion scavenging tests, methanol (0.40 mL) was added to the lignin/sodium hydroxide mixture in the milling vessel. To investigate the influence of the moisture content, water was added to the milling vessel to increase the total moisture content in the sample from its original value of 3.7 wt% to the desired moisture content. Finally, to serve as a control experiment, organosolv lignin samples (1.50 g) and sodium hydroxide pellets (1.50 g) were milled for 1 min at 800 rpm (13.3 Hz) separately, then combined and shaken in the mill without milling balls for 10 s. These samples were left to sit for 5 min–8 h before being prepared for molecular mass analysis.

2.4. Gas chromatography – mass spectrometry (GC–MS) and gas chromatography – flame ionization detector (GC–FID)

The milled samples were dissolved in methanol and diluted to a concentration of 10 mg/mL. The samples were neutralized by addition of hydrochloric acid in an amount equivalent to the sodium hydroxide in the reaction mixture. 3,5-Dimethoxyphenol was used as an internal standard. Samples were filtered using 0.2 μm polypropylene membranes. GC–MS analysis was performed using a Varian (Agilent) 450-GC with a FactorFour[™] VF–35 ms capillary column (30 m \times 0.25 mm \times 0.25 μm) coupled with a 300-MS Varian (Bruker) mass spectrometer (EI, 200 °C). The carrier gas was helium at 1.0 mL/min with an autosampler injection volume of 1.0 μL . The temperature of the column was initially held at 70.0 °C for 1.50 min, then raised at a rate of 35.0 °C/min to 100.0 °C. The temperature of the column was then raised at a rate of 10 °C/min to 300.0 °C, where it was held for 12.0 min.

To obtain more quantitative results for the yields of monomers, samples were simultaneously injected into the same Varian (Agilent) 450-GC equipped with a flame ionization detector (FID) with a split ratio of 20:1. The GC contained the same column and used the same temperature program as the GC–MS method described previously. The FID was set at 300 °C, with a make-up flow of 29.0 mL/min, an H₂ flow of 30.0 mL/min, and an air flow of 300 mL/min. It is noted even with FID the response factors of different compounds can vary notably [40].

Yield of total detected monomeric species was calculated as follows:

$$\text{yield (wt\%)} = \frac{m_{\text{volatile monomers}}}{m_{\text{total reacted sample}}} * 100\% \quad (2)$$

Selectivity of each detected monomeric species was determined as follows:

$$\text{selectivity (wt\%)} = \frac{m_{\text{volatile species}}}{m_{\text{total volatile monomers}}} * 100\% \quad (3)$$

2.5. Gel permeation chromatography (GPC)

The milled samples were dissolved in THF and diluted to a concentration of 4 mg/mL. The samples were neutralized by addition of hydrochloric acid in an amount equivalent to the sodium hydroxide

Download English Version:

<https://daneshyari.com/en/article/6504771>

Download Persian Version:

<https://daneshyari.com/article/6504771>

[Daneshyari.com](https://daneshyari.com)