

Spray Ozonation of Acid Solubilized Lignins to Afford Aromatic Aldehydes

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Highlights

- A novel spray ozonation at ambient temperatures and pressures
- Selectively prunes aromatic aldehydes from lignin's subunits linkers
- Serves to pretreat lignin for further catalytic depolymerization
- Successful with a variety (grasses/softwoods/hardwoods) of lignins

1. Introduction

To best understand the structure of lignin, one must better understand the bonds between both monomer and structural units [1]. Oxidized monomer units serve to link not only lignin subunits, but also join these subunits to neighboring hemicellulose [2]. The olefinic bonds in these hydroxycinnamic acid derivative linkers, along with those retained in partially reacted monolignols serve as important targets in lignin depolymerization distinct from the numerous and diverse carbon-carbon and carbon-oxygen bonds. The ozonation of olefins has been well researched [3,4]. However the challenge of reacting a powerful oxidant with substrates dissolved in the liquid phase poses challenges, including gas-liquid mass transfer limitations and the need to control reactor residence time to prevent unwanted side reactions, typically deep oxidation. Spray reactors have been demonstrated as a powerful way to optimize both mass transfer rates and residence time for fast oxidations [5] Optimizing particle size and residence time allows for oxidations to proceed selectively at ambient or mild temperatures and pressures.

The numerous lignin valorization processes that are being investigated are an indication of the functional diversity of the aromatic polymer and its monomers [1]. For over nine decades, many have sought one of the world's most desirable aroma compounds, vanillin, from wood [6]. The Borregaard company is the last surviving member of a once-booming industry that stripped vanillin from oxidized paper processing waste. The other major aldehyde product from the partial oxidation of lignin is 4-hydroxybenzaldehyde (4HB), vanillin's unmethoxylated counterpart derived from the coumaryl monolignol. 4HB is used as a component in pharmaceutical products, and as an antioxidant in age resistive polymers [7]. In addition, 4HB may serve to become an important platform molecule as a source of aromatics and as a polymer precursor owing to the hydroxyl and aldehyde functional groups. Up to 20 wt% of grass lignins consist of *p*-coumaric and ferulic acids, bound primarily as pendant esters in the C γ -position of the β -O-4 linkages of the polymer. Ozone easily cleaves the C=C bonds that attach the aromatic portion of the hydroxycinnamic acid groups to the polymer, yielding oxoaromatic compounds, including vanillin and 4HB. These value-added monomers should be easily isolated from the product mixture if the bulk of the lignin is left largely untouched by the ozone pretreatment.

2. Methods

A dilute solution of lignin in acetic and formic acid is solubilized in an acetic acid/formic acid mixture. The lignin solution is pumped through a nozzle located at the bottom of a 4L glass spray reactor operated at ambient pressure and temperature. The spray droplets meet a flowing stream of ozone in air. The residence time in the reactor based on the liquid holdup is typically on the order of a few minutes. The liquid effluent from the reactor is collected and analyzed via gas and gel permeation chromatographies to elucidate aldehyde and acid products, and the extent of depolymerization, respectively. The ozone-containing stream is

vented through a solution of sodium hydroxide and hydrogen peroxide in methanol to decompose any remaining ozone.

3. Results and discussion

The main products isolated include vanillin (3-methoxy-4-hydroxybenzaldehyde) and 4-hydroxybenzaldehyde (4HB), with small amounts of the oxidized byproducts, vanillic acid and 4-hydroxybenzoic acid (Figure 1A). For the grass lignin samples, the vanillin yields reach 1.6 wt. % while 4HB yields reach as high as 2.9 wt.% of the lignin fed. The total yield of these two monomers (4.5 wt.%) is significant considering that the concentrations of the pendant groups range anywhere from 12-20 wt.% of grass lignins. As expected, hardwood samples yielded no quantifiable 4HB, and low vanillin yields of approximately 0.48 wt. %. Size exclusion chromatography of different lignins indicates that both plant types depolymerize but to different extents, in part because the lignins begin on very different scales (Figure 1B). As the aldehyde precursors serve to link lignin subunit globules which coalesce at regular masses, the inter-peak distances indicate grass lignin globules may be larger than those of hardwood lignins, as they consist of different monolignols, yet gather at the same molar masses.

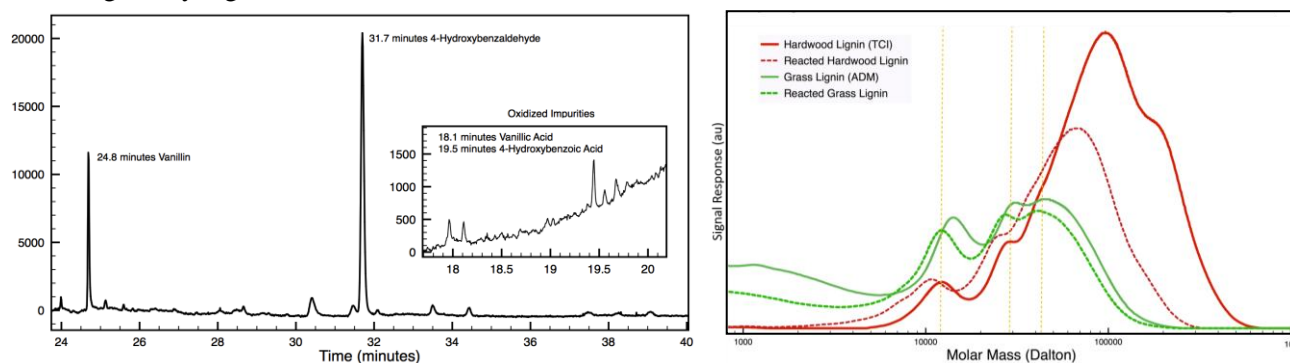


Figure 1. A) Gas chromatography of ozonated grass lignin, featuring the aldehyde and acid products. B) Gel permeation chromatography of hardwood and grass lignins before and after ozonation.

4. Conclusions

A simple spray ozonolysis process was demonstrated to pretreat grass lignins to recover vanillin and 4HB as value-added products. This reactor setup thus prepares various lignins for catalytic depolymerization into aromatic monomers for fuels or as chemicals. Furthermore, the simplicity of the reactor design allows relatively easy optimization of the flow rates to maximize the yields of the desired products. Such results and the extension of this technique to other types of lignins including tannins and nut shell liquids will be presented.

References

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Keywords

Lignin; waste valorization; spray reactor; depolymerization.



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Education

Ph.D in Chemistry with a specialization in Nanotechnology and Material Science at C.U.N.Y. Graduate Center (Awarded June 2016, began 2011)
Received Masters of Philosophy (2014)
American Chemical Society Green Chemistry Summer School Graduate (2015)
National Science Foundation Innovation Corporation Program (March 2013 Cohort)
Graduated Honors B.Sc. in Atmospheric and Environmental Chemistry, minor in English Drama and Theatre from McGill University, Montréal, Quebec (2011)
Enrolled Chemistry Summer School at CPE-Lyon, Advisor C. Corepet (Summer 2009)

Teaching

Lecturer at University of Kansas, Lawrence
Industrial Development of Catalytic Processes (Spring 2017)
at City College of New York, Harlem
Chemistry 272 Organic Chemistry Lab for Majors (3 Semesters) 2012-2014
Chemistry 103 General Chemistry (3 Semesters) 2015-2016
Green Chemistry Education Workshop at University of Oregon (July 2016)
New York Academy of the Sciences Mentor (2011-2012)

Selected Publications

- Silverman, J.R., (2016) Sustainable Molecular Gelators: Beta-D-Glucoside derived structuring agents and their material applications. CUNY Graduate Center, ProQuest, ISBN: 9781369198980
- Silverman J.R., (2016) Biobased Organic Chemistry Laboratories as Sustainable Experiment Alternatives. *J Chem Educ.* doi: 10.1021/acs.jchemed.5b00706.
- Silverman, J.R., John, G., (2015) Biobased Fat Mimicking Molecular Structuring Agents for Medium Chain Triglyceride and Other Edible Oils. *J. Agric. Food Chem.*
- Silverman, J. R.; Samateh, M.; John, G. (2015) Functional Self-Assembled Lipidic Systems Derived from Renewable Resources. *Eur. J. Lipid Sci. Technol.*
- John, G.; Hwang, H.; Jadhav, S.; Silverman, J. (2013). Sweet and Sustainable, Biorefinery concept: a powerhouse for sustainable future and molecular design. *Journal of Chemical Education.* (2014).
- Jung, J. H., Lee, J. H., Silverman, J. R., & John, G. (2013). Coordination polymer gels with important environmental and biological applications. *Chemical Society Reviews*, 42 (3), 924–936. doi:10.1039/C2CS35407A
- R. Hudson, J. Silverman, C. M. Cirtiu, C.J. Li*, A. Moores* (2011) "Copper-Iron-Oxide Nanoparticles as Magnetically Recoverable Catalysts for the Biginelli Condensation" Proceedings of the 3rd International Conference on Nanotechnology, 2012, AUG 7-9, 2012

Research

Center for Environmentally Beneficial Catalysis, Dr. Bala Subramaniam, at KU (2016 - present)
Focus: Waste valorization, spray oxidation of lignin, life cycle analysis, science communication, academic/industry collaboration, safety
Dr. George John's Soft Material's Laboratory, City College of New York

Focus: Organic self-assembly of bioderived materials from renewable resources (2012)

Joined CHEM-392 Development Team under M. Huot at McGill University

Focus: Developing relevant advanced level lab experiments for senior students. (2011)

Completed honors research project under A. Moores, and C.J. Li at McGill.

Focus: Heterogeneous metal nanoparticle catalysis (Summer 2010)

Literature project/presentation under C. Copéret at CPE-Lyon

Focus: Metal-Oxide catalyzed olefin metathesis (Summer 2009)

Selected Conferences and Awards

Lecture at the 6th Workshop of Fats and Oils as Renewable Feedstocks for the Chemical Industry in Karlsruhe, Germany March 17th-19th 2013 entitled: Bio-catalytic synthesis of small molecule oil structuring agents from renewable resources. Session ID: L28. Lecture at 20th Gordon Green Chemistry Seminar, July 30-31st, Stowe Vermont, titled "Sustainable Molecular Oleogels: Next Generation Fuels. (2nd Prize) at the Antioxidant Symposium of the NYSCC June 2014 at the New York Academy of the sciences entitled: Pro-antioxidant oil structuring agents from renewable resources, (NSF Scholar) at the 18th Green Chemistry and Engineering Conference in Washington DC, July 2014 entitled: Sustainable Molecular Oleogelators. Awarded a University of Kansas Libraries Open Educational Resources Grant (2017). Awarded the James Whittam award for research excellence in interfacial phenomenon (2015)

Member of: ACS, AIChE, AOCS, SCC, CM&E, NYAS, KAS, City College Science Alliance

Proficient in: chemical transformations, life-cycle analysis, self-assembly, mechanochemistry, biomass processing, enzyme catalysis, soap making, baking, brewing, experiment and evaluation design

Interests: sustainability, origin of life, materials applications, chemical history, education, theatre, and writing.