

Lignin value prior to pulping (LVPP): An advanced pulping concept

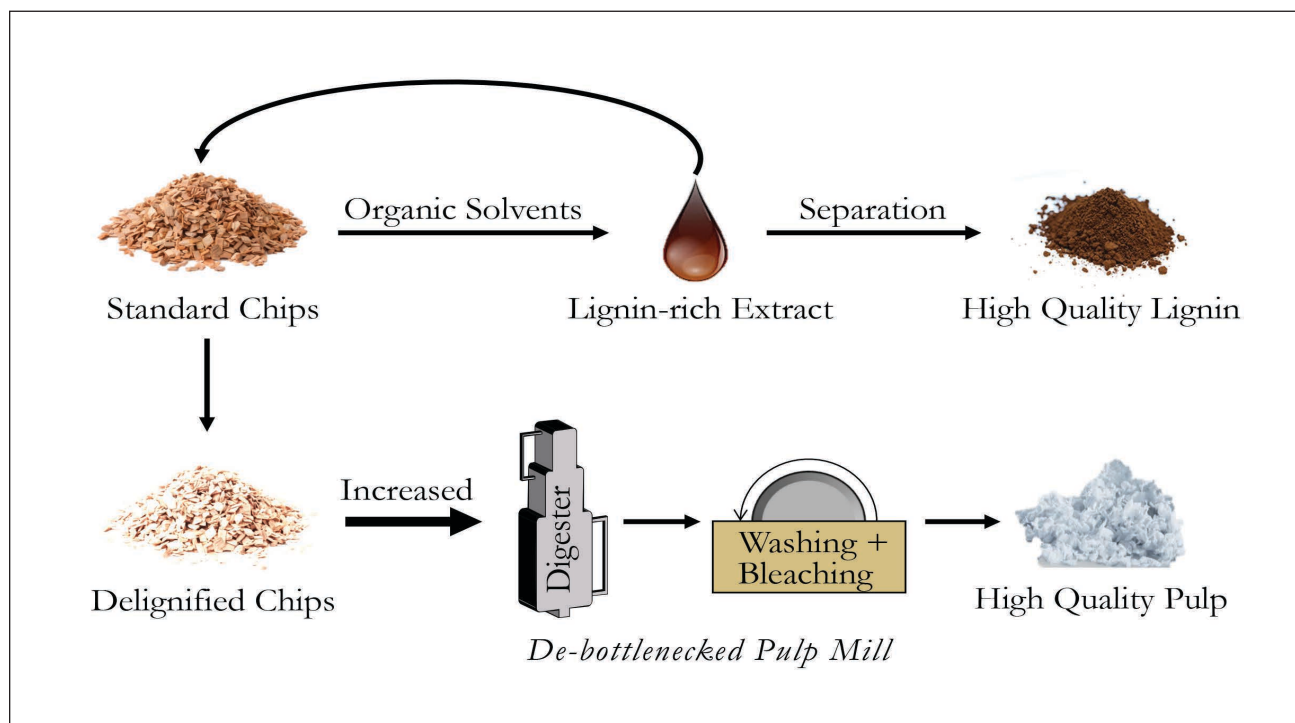
THOMAS T. KWOK, CHRISTOPHER O. LUETTGEN, MATTHEW J. REALFF,
AND ANDREAS S. BOMMARIUS

With an extensive infrastructure of kraft pulp mills, the United States pulp and paper industry is poised to take advantage of the scientific breakthroughs in lignocellulosic treatments. Volatility of oil prices and availability of ethanol subsidies have focused lignocellulosic research on the production of biofuels. Consequently, billions of dollars have been spent to convert biomass to ethanol, focusing primarily on converting cellulose from low recalcitrant, often grassy, feedstocks (e.g. corn stover, sugarcane bagasse, and wheat straw). Discoveries of effective pretreatments, which fractionate agricultural residues into lignin and carbohydrates, have spurred the forest products industry to pursue ethanol from woody biomass, a more recalcitrant feedstock. Though admirable as a concept, the idea of filling our nation's gas tanks with cellulosic ethanol from recalcitrant, woody biomass is naïve at best. The mass value of pulp is double that of fermentable sugars and yields of sugar and ethanol are detrimentally low

when compared with pulping yields per ton of cellulose. Thus, from an economic perspective, pulpwood cellulose is best positioned towards pulp and paper products unless current fuel prices rise substantially.

A byproduct of lignocellulosic research is an enhanced understanding of lignin separation and valorization. Routes to valuable chemicals such as phenol, adipic acid, and vanillin are extensively studied, and lignin extraction techniques are numerous and diverse. We take this knowledge, combined with the understanding that cellulose is most valuable as a pulp, to describe an advanced pulping technology concept called lignin value prior to pulping (LVPP). This process utilizes organic solvent pretreatments to delignify woodchips prior to a kraft chemical pulping process. This advanced system provides an un-sulfonated lignin stream and has the potential to improve the governing economics of a pulp mill (**Fig. 1**).

While similar in concept to the value prior to pulping



1. Lignin value prior to pulping (LVPP): Organic solvent pretreatment increases pulp production and generates a new lignin stream.

SPECIAL FEATURE

(VPP) process introduced in the early 2000s, the extraction of lignin as opposed to hemicellulose has several distinct advantages [1,2]. The VPP process struggles to overcome the small margins that are imposed by pulp losses of 5%–15%, and the early extraction of hemicellulose contributes to significant pulp quality degradation [3-5]. LVPP addresses these issues by relieving bottlenecks to increase pulp yield and maintaining fiber quality with effective organic solvent delignifiers. Thus, LVPP can provide increased value by both increasing pulp throughput and creating an accessible lignin stream for chemical valorization.

The LVPP process will alter several kraft mill unit operations. Specifically, the recovery boiler, the digester, and the evaporator systems will be significantly affected. LVPP processes will also require several additional unit operations. First, a pressurized pretreatment vessel will mix an organic solvent with the wood chips to enable adequate solubilization of lignin. Second, counter-current washers will be employed to displace the organic solvent before the delignified chips are sent to the pressurized digester. Third, a precipitation step will isolate the lignin from the organic solvent. Finally, a separations unit will be added to recover the solvent. These changes will introduce new costs, but these costs are offset by the additional revenue streams.

A RENEWABLE BIOPRODUCTS INSTITUTE PROJECT

In a project supported by the Renewable Bioproducts Institute (RBI) at Georgia Tech and funded in part by Georgia-Pacific, Domtar, and Solenis, we are developing techno-economic models and performing initial lab-scale testing for the LVPP process.

The LVPP process hinges on an effective pretreatment step that isolates lignin from wood chips. An existing body of lignocellulosic research demonstrates how many organic solvents will isolate and modify native cellulose towards the production of cellulosic ethanol [6]. Several organic solvents are particularly good at solubilizing large quantities of lignin from biomass [7-11]. We are optimizing these organic solvent conditions and finding new solvents that quickly penetrate the wood chip, selectively solubilize lignin, maintain a wide liquid state temperature range, are straightforward to synthesize, and feature a low toxicity. After mapping delignification efficiency with cellulose swelling effects, we formulated an economic screening criterion that accounts for environmental impacts as well as for production capacity and separation efficiency [12].

Our techno-economic analyses demonstrate the importance of solvent recovery and determine several bounds on solvent loss. In a first-order economic analysis, we treat lost solvent as a feedstock in a lignin recovery system. With feedstocks accounting for 40% of process costs and a revenue margin set by comparing a lignin selling price with its heat value, we can show that the total solvent loss for our process must be less than 0.5% or 3.0% for a lignin selling price of

\$300 and \$1000, respectively. To account for this loss, we research organic solvent recovery through chip washing, lignin precipitation, and solvent-water separations.

A chip washing unit operation differs from traditional brownstock washing due to the nature of the biomass. Modeled as a porous solid with entrapped liquids, the governing equations for the pore and free liquid solvent concentrations may be described by a linear combination of diffusion equations. These models can direct experiments and will enable the optimization of solvent loss due to chip entrapment.

Our organic solvents are effective delignifiers due to their strong affinity with lignin, so separation from lignin requires a strong anti-solvent or a significant change in conditions to affect the system's thermodynamics. The separation techniques we explore for our LVPP process are anti-solvent addition, membrane separation, and distillation. We use several anti-solvents for lignin, and we model both black liquor membranes and three-component distillation. The implementation of the latter techniques hinges on the extent of fouling caused by the precipitating lignin.

Once the lignin is precipitated and the chips are washed, the second stage of solvent recovery is the separation of the organic solvent from water. Our initial models suggest that distillation is the best option, with preliminary distillation energy loads on the order of 700 kJ/kg of solvent feed. These loads depend on the water content of the feed, the selected solvent, and the desired product streams, so we are still optimizing and exploring other separation techniques.

A CALL FOR RESEARCH

By modeling the pretreatment and solvent recovery, we are able to sufficiently define the LVPP process and test its feasibility. The treated wood chips are easily converted to fibers where yield and quality may be determined. However, it is necessary to quantify how the upstream modification of chip composition and structure impacts the downstream pulping process to realize LVPP's full potential.

Continuous digester models are needed to test our hypotheses that delignified chips will decrease the required cook severities, or H-factor, and decrease the equipment cost per unit volume without significantly impacting liquor flow and compaction due to lighter chips. Recovery boiler lifespan models are needed to understand the impacts of lower heat loads and altered cooking liquor-to-organics ratios. Additional considerations are needed due to the changing chemical compositions to the lime kiln, an altered black liquor to the evaporators, the new chip size distribution to the blow tanks and screens, the decreased lignin for brownstock washing and bleaching, and ultimately the different final pulp characteristics.

Understanding and quantifying LVPP's economic impact on a mill will enable comparison to lignin value after pulping (LVAP) processes. Current industrial lignin production recovers lignin after digester treatment. While easier to separate, this post-digester lignin has come into contact with harsh

alkali chemicals and does not provide bottleneck relief to the mills. The improved mill processes and un-sulfonated lignin streams will justify the increased difficulty of LVPP's lignin extraction. While there are still many parameters to understand, the LVPP process modifications promote a renewable chemical stream while decreasing the fixed cost per ton of pulp produced. A thorough pursuit of the LVPP process will ultimately provide a foundation for optimal utilization of our world's most renewable feedstocks. **TJ**

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ABOUT THE AUTHORS

Kwok is a post-graduate student in the School of Chemical and Biomolecular Engineering and the Renewable Bioproducts Institute; Luettgen is professor of practice in the School of Chemical and Biomolecular Engineering and an associate director of the Renewable Bioproducts Institute; Realff is professor in the School of Chemical and Biomolecular Engineering and an associate director of the Renewable Bioproducts Institute; and Bommarius is professor in the School of Chemical and Biomolecular Engineering, the School of Chemistry and Biochemistry, and the Renewable Bioproducts Institute at Georgia Institute of Technology, Atlanta, GA, USA. Email Bommarius at andreas.bommarius@chbe.gatech.edu.



Kwok



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