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Lignin to plastic opportunities

Under the conditions evaluated by NARA to convert post-harvest forest residuals into biojet fuel, approximately two-thirds of the woody material is left over as a byproduct. This left over material is rich in lignin, a complex polymer molecule found in plant cell walls.

The USDA-NIFA, through the NARA grant, funds research to develop high-value chemicals and materials that can be made from the lignin-rich material left after the various stages of producing biojet fuel from post-harvest forest residuals. Developing these high-value products is an essential part of an economically sustainable supply chain.

NARA researchers have used the lignin-rich material to make activated carbon, cement additives, resins, and feedstock chemicals with the intent to transfer this technology to private industry. As part of this effort, Simo Sarkanen and his team at the University of Minnesota are developing formulations for converting the co-product lignin into bio-plastics. Recently his team published a peer-reviewed paper, partially funded by the USDA-NIFA through NARA, describing the lignin-based plastics developed in their lab, which are distinguished by the highest lignin contents ever reported.

Read Path to Plastics Composed of Ligninsulphonates (Lignosulfonates)

Experimental samples

The authors isolated lignins from two sources. One source came from Jack pine (Pinus banksiana) and the other came from post-harvest forest residuals consisting mainly of Douglas-fir (Pseudotsuga menziesii). The Jack pine lignin was obtained by extracting into solution the lignin from wood that had been milled into a powder. The lignin from post-harvest forest residuals (termed NARA lignin) was obtained after the residuals had been pretreated and enzymatically hydrolyzed. Pretreatment and enzyme hydrolysis are processes used consecutively to liberate the simple sugars from wood so they can be fermented to produce biojet fuel; thus this lignin preparation is similar to the lignin that would be produced in a biorefinery envisioned in the NARA supply chain.

Processes in the NARA supply chain

A fundamental difference between these two lignin samples is that sulfonic acid groups are linked to the NARA lignin due to the bisulfite-based pretreatment process used, whereas the milled wood lignin from Jack pine does not contain sulfonic acids. Lignins possessing sulfonic acid groups are commonly called lignosulfonates or ligninsulphonates.

Experimental design

The authors manipulated the lignin samples so that they combined to form polymeric materials or plastics without small voids in their interior domains. Manipulations of the lignin samples included introducing methyl groups onto the lignin and/or blending with other chemicals or polymers to reduce brittleness. The mechanical properties of the various lignin-based plastics were then compared to commercially available polystyrene and polyethylene, polymers used for packaging and building materials. The authors also examined the lignin-based plastics at the molecular level to see how the molecular lignin components were arranged within these new materials.

Results

The paper describes the first comparison of polymeric materials or plastics based on softwood lignin and lignosulfonates that are either chemically methylated or not methylated. After methylation (introducing methyl groups onto) the lignin from milled Jack pine, the authors produced a bio-plastic containing 85wt% of the methylated lignin that surpassed polystyrene in strength (tensile behavior). Using 85wt% of the unmethylated (chemically unmodified) NARA lignosulfonate, the authors produced a bio-plastic with similar properties to polyethylene. From a commercial perspective, these results demonstrate that a polyethylene substitute can be made from the lignin material generated using the conversion processes optimized in the NARA project.

This work contradicts traditional thinking about what lignin polymers are really like. In the past, materials made with very high lignin content have been quite brittle. The brittleness was thought to be caused by lignin macromolecules being too rigid due to chemical crosslinking (covalent bonding) within the individual polymer chains. To the contrary, the properties of the new plastics, with very high lignin contents, reveal that numerous non-covalent bonds are instrumental in preserving material continuity through the arrangements of individual lignin components at the molecular level. This understanding sets a new course for manipulating lignin for commercial purposes.

Dr. Sarkanen and his colleges have applied for an international patent titled "Compositions Including Lignin" (PCT/US2015/020599) and a provisional patent entitled "Compositions Including Ligninsulfonate, Compositions Including Un-alkylated Lignin, and Methods of Forming" (62/215,017) are partially based on the results from this work.

Extractives found in post-harvest forest residuals

When it comes to evaluating an industry that uses post-harvest forest residuals (slash) to make bio-jet fuel and co-products, the primary components in softwoods, like Douglas-fir, receiving the most industrial interest are cellulose, hemicellulose and lignin. The cellulose and hemicellulose contain the simple sugars used to biofuel and other chemical products. The lignin is a byproduct of the fuel conversion process and can be used to make additional products like activated carbon and plastics. If water is excluded, these three components comprise up to 90% of the wood.

There are a number of other chemical components in softwoods found in much lower concentrations. A collective term for many of these chemicals is "extractives". Extractives include waxes, flavonoids, isoprenoids, tannins and other molecules. These chemicals are located in all softwood tissue types with a higher percentage in bark and needles. Trees produce extractives primarily for biological signaling, defense and metabolism.

There are many reports that describe and quantify extractives in Douglas-fir and many other tree species. From a commercial perspective, there is a marketplace for many softwood extractives used to make solvents and pharmaceuticals. Extractives can, however, interfere with industrial processes used to make paper and chemical products like bio-jet fuel from wood and can also contribute to the toxicity of the waste stream.

In a recent peer-reviewed paper, supported by the USDA-NIFA through NARA, researchers Karl Oleson and Daniel Schwartz, from the University of Washington, provide a review of Douglas-fir extractives and the first quantitative assessment of the extractives found in post-harvest forest residuals (slash), which is the material evaluated by NARA as a feedstock to produce biojet fuel and other products.

Read Extractives in Douglas-fir forestry residue and considerations for biofuel production

Experiment

Using data presented in previous studies that quantify the amount of extractives found in various Douglas-fir tissues like bark, heartwood and sapwood, the authors compute the amount of extractives found in a post harvest forest residual sample (FS-03). FS-03 is used by NARA as a representative slash sample for a Douglas-fir harvest. They then quantify, using an ASPEN model simulation, the amount of extractives expected in product and waste streams generated using the sulfite/bisulfite pretreatment and enzymatic hydrolysis processes optimized by NARA.

Read about the sulfite/bisulfite pretreatment process

Results

Using data from previous analyses performed by NARA researchers, the authors calculate that the FS-03 sample (Douglas-fir forest slash) consists of 23% bark, 33% sapwood and 43% heartwood, and all tissues combined contain 8.08%

extractives. Besides listing and quantifying the varied extractives expected in the FS-03 sample, additional components including water, protein, ash, lignin, poly- and monosaccharides are quantified. As the extractives move through the pretreatment and hydrolysis steps used to produce bio-jet fuel, the ASPEN simulation shows that of the ~8% extractives, 3.579% is retained in the spent sulfite liquor, 0.026% is in the evaporator waste, and 4.685% remains in the sugar stream that is sent to fermentation. The simulation also follows the likely chemical changes that occur as these varied extractives are subjected to the thermal and chemical conditions used during wood to biofuel processing.

Much of the paper reviews the unwanted affects that extractives have on processes used to make biojet fuel from post-harvest forest residuals. For instance, the extractive class proanthocyanidins hinder cellulase activity used to remove simple sugars from cellulose and hemicellulose. Another extractive class, diterpenes, can be toxic to yeast used in the fermentation step that converts simple sugars into isobutanol.

See multiple steps used to produce biojet fuel

Conclusion

This analysis provides an excellent starting point for understanding how extractives found in post-harvest forest residuals can affect processing steps used to create biojet fuel and other chemical products. The information also assists NARA researchers who are optimizing these processes and providing estimates used to determine the amount of volatile and/or toxic emissions created in the supply chain.

The authors also point out knowledge gaps. Extractive quantities are not specified between the two prominent Douglas-fir species (var. menziesii and var. glauca). In addition, the thermodynamic parameters for many extractives molecules have yet to be determined.

Slash removal and microbial communities

A key issue attached to the use of post-harvest forest residuals (slash) to make biojet fuel and other chemical products is how slash removal impacts the productivity and ecology of a working forest. The USDA-NIFA, through the NARA project, funds research to evaluate the impacts of slash removal on soil, wildlife, air, and water quality. NARA researchers have published multiple peer-reviewed reports that evaluate how soil nutrient levels are maintained and effectively measured, and additional studies will be published soon that focus on wildlife, soil temperature and water quality.

Recently a peer-reviewed study, funded by the USDA-NIFA through NARA, was published that evaluates how slash removal treatments affect soil microbial populations and diversity. It is anticipated that changes in soil microbial ecology could provide an early warning system for potential long-term impacts on forest watersheds and food webs.

Understanding the consequences of land use changes on sustainable river basin management in the Pacific Northwest, USA.

Experiment and results

The authors obtained soil samples from the NARA long-term soil productivity (LTSP) site located on Weyerhaeuser land near Springfield Oregon. This site contains 28 one-acre plots that were harvested for timber and treated with different compaction intensities and varied levels of slash removal. The treatments are used to evaluate how soil compaction and slash removal affect soil temperature, tree growth, pollinators, and microbial diversity.

View this webinar to learn more about the NARA LTSP site and the multiple studies conducted there.

Multiple soil samples were obtained from each treatment plot plus from a non-harvested section near by, and the DNA contained in each soil sample was extracted and used to identify the number of microbial communities in each sample. The results indicated no statistical difference in the number of microbial populations between treatments.

The authors also observed that the total amount of DNA from each sample varied significantly. This variation was observed even among samples taken in plots that contain a similar treatment. Additional evaluations of soil type are underway to explain the variable DNA concentrations.

Conclusions

The results presented in this publication suggest that the varied compaction and slash removal treatments did not affect microbial diversity. The authors intend to develop the microbial DNA testing method further so that it could be used to predict long-term changes to water quality and nutrient levels. To do this, they intend to use the DNA in the samples to identify individual microbes with the soil community and note those microbes that are responsible for nitrogen and phosphorus cycling. Soils with abundant or deficient numbers of these microbe types should affect water quality in different ways.

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