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NARA's 2014 peer-reviewed publications

In 2014, NARA researchers published 25 papers in peer-reviewed journals. These publications help transfer NARA research to a wide audience. Here is a brief narrative to how these peer-reviewed papers complement NARA's goals and contribute towards evaluating the use of forest residuals as a feedstock to produce chemical products.

NARA goal 1: Sustainable Biojet

A number of papers were published that should help land managers, haulers and logging contractors reduce the cost of moving biomass from slash piles to a conversion facility. Methods to increase truckload density (1), measure the amount of biomass in slash piles (2), and tools to optimize biomass processing and transport (3) were provided.

In the conversion scenario being evaluated by NARA, wood-based simple sugars are extracted through process known as pretreatment and enzymatic hydrolysis and then converted into isobutanol and other chemical products like biojet fuel. NARA researchers published papers that evaluate the performance of sulfite-based (4), (5) and dilute acid (6), (7) pretreatment procedures and on enhancing enzymatic hydrolysis (8). An alternative technology to the sugar-to-isobutanol pathway was presented that converts the simple sugars into volatile fatty acids, many of which have commercial applications (9). Contributions were also made towards understanding how biofuels can be derived from pyrolysis (10).

Long-term efforts to help softwood tree-breeders select future seedlings that benefit traditional timber use and a biofuel and co-product industry were advanced. Two publications describe how phenomics technology can screen large numbers of conifer seedlings for drought and salinity resistance (11), (12). Another publication showed strong evidence that some trees release their simple sugars during pretreatment better than others and that this characteristic is genetically controlled (13).

NARA goal 2: Value Lignin Co-Products

Using the simple sugars from wood residuals to make valuable products leaves a wood byproduct containing a high percentage of lignin. Developing commercial products from the lignin-rich material is an essential component to developing an economically sustainable industry. One publication introduced a method to break-up the lignin molecules (depolymerize) into structures that could more readably be converted into valuable chemical products (14). Other publications described methods to convert the lignin-rich material into epoxy resins (15) and dicarboxylic acids (16).

NARA goal 3: Rural Economic Development

The NARA project is based on the assumption that a wood residuals-to-biofuel and co-product industry and the connected economic development will succeed only if it is socially, economically and environmentally sustainable. To better gage environmental sustainability, publications were produced that evaluate the impact of forest residual removal on soil nutrients (17), (18) and soil compaction (19). Additional publications evaluated the effects of using nitrogen fertilizer on plantation forests (20) and methods to measure soil productivity (21). A significant output tasked to NARA is to develop a comprehensive life cycle assessment (LCA) that compares the greenhouse gas emissions generated from the wood residuals-to-biojet and co-products supply chain to a jet fuel and co-product supply chain based on fossil fuels. This assessment is still in development; however, the first peer-reviewed publication that addresses the methodology used is available (22).

NARA goal 4: Supply Chain Coalitions

Identifying, informing and involving the individuals, businesses and communities who will use NARA's research to implement a supply chain that develops chemical products from forest residuals is a key component to the project. NARA is developing tools to help stakeholders identify the best locations for depots and biorefineries. One publication outlines a developing method used to rank communities not only for their physical assets and location but also for their likely social acceptance to participate in the emerging supply chain (23).

NARA goal 5: Bioenergy Literacy

Publications that describe NARA's efforts to enhance the bioenergy literacy of students, educators, professionals and the general public include an evaluation of methods used to gage the effectiveness of the Imagine Tomorrow competition on high-school student's literacy and career choices (24) as well as a lesson plan for middle school students comparing carbon sequestration to forest products (25).

Other NARA publications

The purpose of this article is to highlight the 2014 peer-reviewed journal articles produced by NARA researchers and place them with the context of NARA's five goals. In total, 46 peer-reviewed articles have been published since NARA's inception and numerous other publications have been produced which are listed on the NARA website.

View here for a listing of all NARA produced articles, technical reports, book chapters, educational materials, theses and conference proceedings to date.

View NARA progress reports

View supply chain analyses

References

Listed below are the publications referred to in this newsletter entry with links to the journals. Many of these articles are further described in previous NARA newsletters.

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Image from Effects of High Speed Blowing on Bulk Density of Ground Residuals

Packing forest residues for transport

Transporting a low value product like forest residuals from a timber harvest site to a processing facility represents a significant economic and logistical challenge for a wood to biofuel supply chain. One way to ensure that transport costs are as low as possible is to maximize the amount of wood residuals carried per trailer load.

Placing ground wood residuals (chips) into a trailer sounds pretty simple — just fill up the trailer to legal weight and go. However, trailers carrying dry wood chips that contain less than 35% moisture content generally do not exceed weight restrictions when filled, which makes the load volume limited. In this case, there is opportunity to carry additional wood residuals per load if the load density can be increased.

In a recent paper published in the Forest Products Journal and funded by NARA, authors Rene Zamora-Cristales, John Sessions, David Smith and Gevan Marrs analyze methods to increase the density of wood chips per trailer load.

Read *Effects of High Speed Blowing on Bulk Density of Ground Residuals*

Two grades of wood chips considered

Two feedstock size classes were used for this evaluation: Douglas-fir branches-and-tops and larger, thicker pieces commonly called pulpwood. Both feedstocks are commonly found mixed in timber harvest slash piles. Depending on market conditions, pulpwood is selectively removed or excluded from slash piles and used to produce higher value products. The average moisture content for the branches-and-tops was 17.3%, and the bark content was 15.7%. The average moisture content for the pulpwood was 20.12% and the bark content was 4.4%. Both feedstock classes were reduced in size using a horizontal grinder equipped with 7.61 cm screens followed by 10.16 cm screens.

Loading method and bit type

The study evaluated two factors that contribute to wood chip bulk density: loading method and bit type. For loading method, the study blew residual grindings vertically into the trailer at high speed (~120 mph) and compared these results to a more standardized method of loading where grindings are dropped into the trailer from a conveyor belt.

What they found was that the high speed blowing increased the load's bulk density by a range of 24% to 35% over conventional loading. The variation in density improvement depended on the feedstock and on the bit types used. To put this into economic perspective, the authors calculated that the increased bulk density could cut delivery costs by $8.3 per ton for branches-and-tops and $14.7 for pulpwood on a 200 km trip.

As mentioned, the type of bits used with the grinder could impact load density. Ether carbide hammer bits, knife-edge bits, or a combination of the two were installed on the grinder. According to the authors, "Carbide-coated hammer bits have relatively blunt edges that are highly abrasive and tend to hammer shred the material. Knife-edge bits tend to cut shred the residue using the sharp edge of the bit. Carbide hammer bits tend to produce less dense material compared with knife-edge bits, but they are less susceptible to contaminants." Turns out that knife-edge bits did improve the bulk density of pulpwood over carbide-coated bits, however, bit selection did not influence the bulk density of branches-and-tops.

Research contributions

As stated in the paper, "Although extensive research was found in the horizontal blowing of chips, few studies were found that applied directly to grinding operations, and no research was found in relation to high speed blowing of grindings in a vertical orientation during loading."

They conclude their investigation by pointing out that even though the use of high speed blowing can increase load density significantly, other considerations such as ease of unloading and blower costs will need to be considered to evaluate overall cost savings.

Dilute acid pretreatment on Douglas-fir residuals

Pretreatment is a procedure used to disrupt the chemical bonds that hold cellulose, lignin and hemicellulose (three structural macromolecules in wood) together. The process exposes the cellulose polymers so they can be broken down into simple sugars. Those simple sugars serve as the feedstock molecules for a host chemical products including isobutanol.

It takes a good deal of energy to break the bonds holding lignin and cellulose together, which makes the pretreatment step relatively tricky and expensive. Consequently, NARA has evaluated multiple pretreatment options to help industry select the best protocol to convert forest residuals into chemical products.

The pretreatment protocols evaluated by NARA to date include sulfite-based pretreatments (SPROL and mild bisulfite), wet oxidation, wood milling and dilute acid. In 2014, NARA chose the mild bisulfite pretreatment as the protocol used to develop a wood-to biojet life cycle assessment and techno-economic analysis. The mild bisulfite pretreatment will also be used to generate 1000 gallons of biojet fuel in 2015.

NARA researchers used the dilute acid pretreatment protocol to rapidly screen Douglas-fir samples for levels of recalcitrance. The dilute acid pretreatment protocol is relatively simple and low cost and has been used extensively as a benchmark method to deconstruct cellulosic materials in grasses and hardwoods.

In a recent paper funded by NARA, researchers based at Washington State University-Tri Cities evaluated the dilute acid pretreatment method on forest residuals and comparatively clean wood chips. The paper provides detailed accounting for sugar yields and inhibitor concentrations culminating in a complete mass balance for pretreatment and enzyme hydrolysis.

> Read *Dilute Acid Pretreatment of Douglas Fir Forest Residues: Pretreatment Yield, Hemicellulose Degradation, and Enzymatic Hydrolysability*

Feedstock characterization

First step was to evaluate the chemical composition of the samples. The researchers used the feedstock samples that were collected early in the NARA project for all pretreatment and fermentation experiments. Sample FS-01 consists of Douglas-fir pulp chips taken from a chip pile at the Weyerhaeuser Longview pulp mill. Sample FS-03 was collected from a roadside slash pile in Northwest Oregon and consists of 87% Douglas-fir, 6% hardwood and 7% other softwoods. Sample FS-10 was collected from a roadside slash pile in southwest Oregon and contains 64% Douglas-fir, 15% hardwood and 21% other softwood species.

Turns out that the FS-01 (pulp chips) had the highest cellulose content (44%) and the least amount of lignin (27.7%) compared to the two forest residual samples. The forest residual samples contained more bark (3.4%) compared to the pulpwood (1.4%). The additional bark in the forest residual samples would partially account for the lower cellulose and higher lignin values.

Dilute Acid conditions

The sweet spot for dilute acid pretreatment temperature exists between 135°C to 210°C. Pretreatment is ineffective below this temperature range, and simple sugars degrade above 210°C. The pretreatment temperature chosen for this study was 200°C. In addition, the reaction time was 30 minuets and 1% sulfuric acid (H_2SO_4) was added. The researchers' intent was to set pretreatment conditions so that a maximum amount of glucose would be released during enzymatic hydrolysis from which they could compare results between the pulp chips and the forest residuals.

Glucose yield

One of the parameters used to measure pretreatment effectiveness is glucose yield. Glucose is liberated from the cellulose fibers when specialized enzymes called cellulases are applied after pretreatment. If pretreatment is successful, then the wood's cellulose is exposed and the cellulases are able to remove glucose. Glucose yields were 68%, 59% and 53% for FS-01 (pulp chips), FS-03 and FS-10 respectively. These yields are relatively low when compared to other pretreatment protocols, which can achieve yields up to 90%. When the solid material from dilute acid pretreatment was milled prior to enzymatic hydrolysis, then glucose yields improved to 86.6% 69.0% and 55.6% for FS-01 (pulp chips), FS-03 and FS-10 respectively. An interesting finding was that the commercially available hydrolysis enzyme mixture contained a small amount of primary sugars. These sugar amounts had to be subtracted from the total sugar yields or otherwise would have increased yields by 5-6%.

Inhibitor formation

High heat and extreme pH levels can change the structure of molecules. Often, these conditions will produce molecules, like organic acids and furfural from sugars and phenols from lignin, that inhibit enzyme function and fermentation. Up to 20% of the initial weight of wood material can be converted into inhibitory compounds depending on the treatment severity. Therefore, the authors evaluated the effect of pretreatment time, acid dosage and temperature on inhibitor levels. What they found is that inhibitor levels increased dramatically when sulfuric acid (H2SO4) levels increased above 2% or if the reaction temperature increased from 180°C to 200°C.

Potential wood characteristics leading to lower sugar yield

The results from this study showed that clean pulp chips responded more favorably to dilute acid pretreatment and hydrolysis than forest residuals. Factors such as high bark content, knots, ash content and bulk density characterized the forest residual samples and probably contributed to their lower sugar yields. The authors point out that effective pretreatment strategies for forest residuals will need to address these characteristics.

This paper presents a thorough evaluation of the dilute acid pretreatment procedure on forest residuals and provides a baseline to compare other pretreatment protocols.

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