Project Title: Hemicellulose Pre-Extraction For Fluff Kraft Pulp Production

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PROJECT OBJECTIVE:

The objective of this project is to develop viable methods for extracting hemicelluloses from SW chips prior to kraft pulping providing fluff pulp manufacturers:

- Pulps with reduced bonding properties
- A new hemicellulose resource stream that could be marketed to the burgeoning biofuel industry.
- Enhanced kraft pulping operations.

This project builds on the current success of preliminary hemicellulose pre-extraction studies by Ragauskas et al.[1] which have identified acidic and alkaline extraction conditions for the pre-extraction of wood hemicelluloses for southern SW. These studies established the general viability of this proposed technology. This project will tailor the hemicellulose pre-extraction process for SW fluff pulps production.

This project directly address key research needs of the forest products industry as stated in AFPA Agenda 2020 research vision which states that the industry needs to better utilizing its raw materials for higher value products. The pre-extraction of hemicelluloses from wood has been identified by the AFPA CTO committee as a key component in the evolution of the kraft pulp mill which maximizes profit from the conversion of wood into cellulosic materials and secondary products including renewable energy. The proposed research plan is also in line with the Institute's research emphasis on "Better Utilization of Wood for Non-Fiber Materials, Chemicals, Fuels, and Energy - Biorefinery."

PROJECT BACKGROUND:

Traditional pulp and paper producers are facing increasing competition from off-shore tropical pulp manufacturers that have low cost wood and labor advantages. To remain viable, the traditional pulp producers have begun to explore new opportunities to increase revenue by producing biopower and other biomaterials in addition to pulp and paper. This proposal seeks to establish the operational data needed to facilitate the development of hemicellulose pre-extraction technologies to develop a new wood biomass resource for **improved fluff** and biofuels production.

The loss of select wood polysaccharides during kraft pulp production is a natural outcome of kraft pulping conditions. Kraft pulping of softwood leads to an extensive removal of glucomannans.[4] During kraft pulping, these extracted hemicelluloses are degraded into low-value isosaccharinic acids,[5,6] and subsequently concentrated and incinerated with extracted lignin in a recovery furnace. The hemicelluloses extracted prior to kraft pulping can be viewed as a natural resource for: (1) Bioethanol production; (2) A valuable papermaking additive.
Studies in the Institute's Fiber Modification/Fiber Fiber Bonding have already demonstrated significant strength benefits by "returning" high DP sugars back to the pulp fiber after pulping. It is further anticipated that the pre-extraction of these "waste" hemicelluloses prior to kraft pulping could substantially improve pulp mill operations by:

1. Enhancing kraft cooking liquor impregnation and improving the overall kraft pulping process for fluff kraft pulp production
2. Improving pulp production capacity for recovery furnace limited kraft pulp mills.

The pre-extraction of hemicelluloses from wood has been studied and practiced for the production of dissolving grades of pulps,[7] mainly through acidic or water prehydrolysis of wood prior to kraft pulping.[8] Gustavsson et al. examined the application of an initial pH 1.4 prehydrolysis of mechanically refined *Populus tremula* followed by a series of differing alkaline extractions which provided a 9% yield of polymer 4-O-methylglucuronoxylan after ultrafiltration.[9] The extraction of wood hemicelluloses with sodium, potassium and lithium hydroxide has also been examined. However, these studies are frequently accomplished with delignified holocellulose or kraft pulps. The pre-extraction hemicelluloses from SW wood prior to kraft pulping without detrimental effects for fluff pulp production remains an unaddressed, technological opportunity.

In preliminary studies, we have identified hemicellulose pre-extraction technologies for SW wood chips. Key finding of this study included:

- Steam pretreatments are ineffective at pre-extracting southern SW hemicelluloses
- Low temperature alkaline extractions (80 – 130 ^{o}C) removes only low levels of hemicelluloses (i.e., <3%)
- Alkaline extractions at 100 – 160 ^{o}C with 1.0 – 1.5% NaOH has yielded 1 - 3% hemicelluloses
- Acidic extractions at 150 ^{o}C with 0 – 0.5% H_2SO_4 provides ~5 – 12% mass recovery of hemicelluloses
- A room temperature acid pretreatment of SW wood chips for 24 h enhances the efficiency/selectivity of hemicellulose extraction by 10 -18%

For fluff production, the bonding potential of SW kraft pulps is frequently excessive. This program addresses this issue by extracting select hemicelluloses from softwood chips prior to kraft pulping. Two competing pre-extraction technologies (i.e., mild acidic vs. alkali with borate additive) will be evaluated for hemicellulose removal and recovery.

This research will provide the technological basis from which a modern fluff pulp mill will evolve into a forest biorefinery producing value-added biofuel resources along with fluff pulp. This proposal will address key process issues including:

- Efficiency and selectivity of hemicellulose extraction from dominant softwood species for kraft fluff pulps
- Pulping and bleaching performance of pre-extracted SW
- Effectiveness of hydrolyzing and fermenting extracted hemicelluloses.

The need for this type of technology has been clearly articulated in public policy. In the U.S.A., bioethanol currently contributes ~4% to the total transportation fuels mix and ~0.01% is based on biodiesel. The Reliable Fuels Act requires that all motor fuels sold by a refiner, blender, or importer to contain 5% a renewable fuel. As outlined in the USDA-DOE 'Billion Ton' report and co-PI's publication titled "The Path Forward for Biofuels and Biomaterials" in Science, [10] America's agriculture and forestry residues have the potential to address approximately a third of this nation's current petroleum demand.[11]

DELIVERABLES:

The deliverables of this research program include:

1. Optimized mild acidic vs. alkaline borate hemicellulose pre-extraction technologies for SW wood
2. Chemical characterization of extracted hemicelluloses, (i.e., molecular weight distribution, components profiles) and control/extracted wood chips (i.e., lignin, carbohydrates contents/structures)
3. Properties of bleached kraft fluff pulp from the control and pre-extracted wood chips, including: FQA, bleachability/refinability (OR is this , absorbency rate/capacity, and bulking capability.
4. Efficiency of hydrolyzing and fermenting extracted hemicelluloses to bioethanol.
5. An evaluation of alkaline pre-extracted hemicelluloses as a papermaking aid.

This program will identify practical hemicellulose pre-extraction technologies for SW wood targeted for kraft fluff pulp production. In addition, this program will provide an assessment of the ***extracted hemicelluloses*** as a ***papermaking resource*** and/or a resource for ***bioethanol***.

VALUE OF DELIVERABLES:

A modern kraft fluff pulp mill could produce ~35,000 gallons/d of ethanol via hemicellulose extraction. The potential net revenue from extraction of hemicellulose prior to pulping has been estimated to be $3.3 billion for the US pulp and paper industry.

It is further anticipated that the pre-extraction of SW hemicelluloses prior to pulping for fluff could substantially improve pulp mill operations by:

- Enhancing kraft cooking liquor impregnation
- Improving the overall kraft pulping process
- Improving pulp production capacity for recovery furnace limited kraft pulp mills.

PROJECT GOALS:

This program is directed at optimizing acidic and alkaline pre-extraction technology for SW fluff kraft pulp. The chemical nature of the pre-extracted hemicelluloses will be established. The extracted hemicelluloses will be employed to evaluate its application for biofuels generation and/or papermaking additives. The pre-extracted pulps will be benched marked against control pulps (i.e., non pre-extracted woodchips) according to their physical properties. *A key consideration of this program is the improvement of kraft pulping operations while at the same time providing yielding new value-added materials.*

Upon completion of these studies, we will provide our program sponsors:

- Optimized hemicellulose pre-extraction technologies for SW kraft fluff pulp
- Physical properties analysis of the fluff pulp made from control and pre-extracted wood chips
- An evaluation of the pre-extracted hemicelluloses for bioethanol production and/or a papermaking aid
- Preliminary assessment of impact of pre-extraction process on kraft fluff pulping operations.

APPROACH:

Pre-extraction: The proposed hemicellulose pre-extraction technologies will be optimized to maximize removal of hemicelluloses typically "lost" during kraft pulping. Pre-extraction conditions will include acidic (i.e. H_2SO_4 0.0 – 0.5%; 120 -150 ^oC and alkaline borate conditions (i.e., 0.01 – 5.0% charge). The

pre-extraction effluents will be characterized according to % mass recovery, the chemical structure of the sugars, lignin, and extractives extracted. The extracted and control woodchips will be analyzed for carbohydrates, lignin content/structure.

Kraft pulping and bleaching: The control and pre-extracted wood chips will be subjected to kraft pulping ***without washing*** to kappa #of 30-20. The kraft brownstocks will be ECF bleached to produce bleached fluff pulp, according to cooking and bleaching parameters relevant to the mill operations of the sponsors of the program. The brownstock pulp will be analyzed for freeness, FQA and kappa #. The control and pre-extracted bleached fluff pulp will be analyzed for physical properties, including: FQA, freeness, defiberization energy, absorbency rate/capacity, and bulking capability.

Hydrolysis and fermentation to ethanol: The extracted hemicelluloses will be enzymatically hydrolyzed to monosaccharides and sugar conversion efficiencies will be determined using HPLC analysis. After enzyme hydrolysis, the liquid hydrolyzates are recovered and used for bioethanol production via fermentation with *Saccharoyces cerevisiae* following standard literature procedures.[12] The "quality" of pre-extracted hemicelluloses for ethanol production will be ascertained by standard literature fermentation to ethanol procedures.

Hemicellulose as a papermaking aid: The extracted alkaline MW hemicelluloses will be evaluated as a papermaking aid. This will be assessed by applying high DP hemicelluloses back onto kraft brownstock pulps and evaluating yield and strength enhancement properties.

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