

ACCESSION NO: 1014753 **SUBFILE:** CRIS
PROJ NO: WNP00002 **AGENCY:** NIFA WN.P
PROJ TYPE: HATCH **PROJ STATUS:** NEW
START: 07 DEC 2017 **TERM:** 30 SEP 2022

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SCIENCE AND TECHNOLOGY FOR THE VALORIZATION OF FOREST AND AGRICULTURAL RESIDUES FOR ALTERNATIVE JET FUEL AND POLYMERS PRODUCTION

NON-TECHNICAL SUMMARY: The bio-economy for the production of fuels, chemicals and materials from underutilized resources has emerged as an important USDA priority because of its tremendous potential for economic growth and its many other societal benefits. The overall goal of this project is to advance the science and technology required to implement a novel biomass economy, for the production of alternative jet fuels and bio-products from the underutilized agricultural and forest biomass resources of Washington State. This project will develop strategies to improve biomass pretreatment, enzymatic hydrolysis and pyrolysis to produce jet fuels and chemicals with materials available in Washington State. The development of new co-products and their incorporation within the context of integrated biorefineries processing will also be explored. Techno-economic and environmental evaluations of bio-refinery alternatives that use the targeted technologies (enzymatic hydrolysis and pyrolysis) and that take advantage of existing infrastructure will be evaluated. The results of this project will be disseminated in workshops, conferences and outreach activities with our agricultural, forest and municipal waste stakeholders in the Pacific Northwest. Additionally, several peer reviewed manuscripts will be published.

OBJECTIVES: The overall goal of this project is to advance the science and technology required to implement a novel biomass economy, for the production of alternative jet fuels and bio-products from the underutilized agricultural and forest resources of Washington State. The specific objectives of this proposal are: Development of new knowledge to improve the performance of pretreatment and biochemical conversion steps to utilize regional biomass to produce jet fuels and chemicals. Development of new knowledge to improve the biomass pyrolysis pathway for the production of jet fuels and chemicals. Development of new co-products to improve the economic viability of alternative jet fuels Techno-economic and environmental evaluation of bio-refinery alternatives that take advantage of existing infrastructure and the production of co-products to improve the performance of standalone alternative jet fuel production concepts. Catalyze technology transfer and develop business models for establishing a jet fuel and bio-products industry in Washington State.

APPROACH: Biomass Supply chain and Pretreatment: This research effort aims at developing a sustainable biomass pretreatment process that reduces the processing cost for liberating sugars

from lignocellulosic biomass, thus improving economics of cellulosic based biofuels. Two strategies will be explored: (1) Hot water treatment and (2) biomimicry approach. Hot water treatment: Will focus on understanding aqueous biomass interactions at various temperature and pressure combinations as a first step to characterize a water-based pretreatment options. In this task we will study water solvation effects on biomass reaction kinetics, mass transfer, and solubility. We will clarify the relationship between pretreatment conditions and process configurations to explain how pretreatment conditions affect total sugar and lignin yields from biomass. The basis for reliable scale-up of existing and novel pretreatment technologies that are vital to reducing the risk for commercial applications will be improved. We plan to study cellulose surface layer conformation via our invented Total Internal Reflection Sum Frequency Generation Vibrational Spectroscopy (TIR-SFG-VS) to advance our understanding of: (1) physical and chemical features of biomass that influence recalcitrance with regard to both changes in biomass structure as a result of reduced recalcitrance phenotypes, and (2) changes of biomass properties during pretreatment and the impact of such changes on plant cell wall microfibril-cellulase interactions during the conversion processes. Biomimicry approach: We will accomplish this task by building upon previous work studying how biological systems in nature such a white-rot fungi and termite degrade plant cell wall. We have discovered that the biological systems employ radicals for deconstruction of lignin. Our work under this effort will include two phases: the first one is to design a radical based system and prove the concept at the laboratory level; the second phase is to incorporate the radical based pretreatment process into a complete system for utilization of lignocellulosic biomass for scaling up and commercialization. Specially designed cell factory: The cellulosic sugars produced from the above efforts will be converted to biofuels and biochemicals. Such conversion will be done biochemically using microorganisms. We have developed a synthetic biology platform using *Yarrowia lipolytica*, an oleaginous yeast that has high capacity for synthesizing lipid based chemicals. In this project we will design *Y. lipolytica* to different cell factories by installing special pathways for target biofuel and biochemical molecules. Examples of these molecules include monoterpenes, sesquiterpenes, fatty alcohols and dicarboxylic acids. Developing algal based aviation fuel: Under this research effort, we will investigate mixotrophic growth mode as an effective way to increase productivity, explore high-value coproduct possibilities to lower the cost of algae-based biofuels, and develop a sequential hydrothermal liquefaction process for fractionating algal biomass to different products. We will also conduct techno-economic analysis for algae-based biofuels and bioproducts. Fundamental studies of biomass thermochemical reactions: These studies will be conducted to understand the relationship between some physico-chemical parameters like crystalline structure and degree of polymerization of cellulose, hemicelluloses and lignin and the composition of the products resulting from their thermo-chemical reactions. Development of new strategies to characterize bio-char and engineering strategies to produce environmental adsorbents. The working hypothesis of this task is that experimental studies with commercially available model compounds and density functional theory (DFT) calculations of unknown compounds will be very useful to inform new deconvolution strategies for the analysis of XPS, Raman and NMR spectra derived from cellulose, hemicellulose, lignin and proteins. These new deconvolution strategies will allow us to identify and quantify structures relevant for the removal of pollutants. Development of new methods to characterize the chemical composition of bio-oils: New hybrid analytical approaches based in GC/MS, GC-FID, UV-Fluorescence, HPLC, LC-MS, TG-MS, Py-GC/MS, GPC, NMR, Karl Fischer titration, solvent extraction and precipitation techniques will be proposed to quantify the content of individual compounds, the content of functional groups and the content of chemical families present in bio-oils. Testing of new concepts to refine bio-oils: New bio-refinery concepts will be tested at laboratory scale to transform crude bio-oils into new transportation fuels. Our team will first focus on the development of solvent extraction separation techniques followed by product development. The proposed bio-refinery targets the production of high value products from C1-C4 molecules (acetol, hydroxyacetaldehyde, and acetic acid), pyrolytic

lignin, pyrolytic humins, and anhydrosugars. Develop lignin-based polymer materials: Lignin-based thermosets and thermoplastic polymer blends with high lignin content, for example, with 50 % or higher lignin loading will be pursued. Improving the compatibility of lignin with other polymers is the key for quality products. We will explore a novel, effective and eco-friendly method for lignin modification, for example, modification of lignin in solid-state reactions, in aqueous medium, etc. Explore new synthesis methods and applications of bio-based self-healing polymers: In this project, we plan to develop high performance self-healing thermosets based on the mechanism of vitrimer using abundantly available vegetable oils as feedstocks. We will select use of vegetable oil, rosin, dienophiles, lignin and other renewable chemicals and oligo polymers as feedstocks for the preparation of biobased self-healing polymers and build the structures of the polymer on reversible Diels-Alder addition and transesterification reactions. Explore biobased hydrogels: In this project, we plan to develop the preparation of biobased hydrogels using renewable chemicals and natural polymers and explore applications of biobased hydrogels in medical dressing materials, agriculture and other industrial products. Depending on the particular applications, the hydrogels will be synthesized using hemicellulose (HC), soy protein (SP), lignin, arginate and/or some monomers. Design cases: Our team will build design cases for novel standalone Alternative Jet Fuel technologies, important industries (sugarcane, pulp and paper, corn ethanol and petroleum refineries), and design cases for targeted co-products that could improve the economic viability of AJFs. Evaluation of the most promising bio-refinery concepts for AJF production. In this task we are using the design cases of existing infrastructure, AJF production technology and co-products identified to generate new bio-refinery concepts for Petroleum Refineries, Pulp and Paper Mills, Sugarcane Mills and dry corn mills. Each of the bio-refinery concepts proposed will be evaluated. The results from this effort will allow us to identify and select the most commercially feasible bio-refinery concepts. Major technical gaps/barriers toward commercialization of each of the bio-refinery concepts will also be revealed from the results of this study. Our team will write proposals to obtain external funds for this study.

KEYWORDS: Bio-economy, bio-refineries, bio-products, bio-fuels
