2015 S-1041 Science and Engineering for a Biobased Industry and Economy

Stakeholder Perspectives on the Bioeconomy

Poster Symposium Abstracts
Oral Presentation Abstracts

Oral and poster presentations at the S-1041 annual meeting
August 10-11, 2015
Ohio Agricultural Research and Development Center
Wooster, OH

Encompassing poster presentations enables students, researchers and policy makers to establish cooperative endeavors for future collaborations.

Poster Symposium Coordinators

Yebo Li, Ohio State University
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The S-1041 Website

A complete description of the S-1041 multistate project, objectives and an electronic version of these abstracts can be found at:
http://oardc.osu.edu/s1041

2015 S-1041 Science and Engineering for a Biobased Industry and Economy Poster Symposium Abstracts Oral Presentation Abstracts

Oral and poster presentations at the S-1041 annual meeting on 10 and 11 August, 2015
Ohio Agricultural Research and Development Center, Wooster, OH

S-1041 Objectives

Develop deployable biomass feedstock supply knowledge, processes and logistics systems that economically deliver timely and sufficient quantities of biomass with predictable specifications to meet conversion process dictated feedstock tolerances.

Investigate and develop sustainable technologies to convert biomass resources into chemicals, energy, materials and other value added products.

Build modeling and systems approaches to support development of sustainable biomass production and conversion to bioenergy and bioproducts.

Identify and develop needed educational resources, expand distance based delivery methods and grow a trained work force for the biobased economy.

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Proceedings edited by
Kent Rausch and Mike Tumbleson

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S-1041 Symposium Background

During the 2009 S-1041 meeting in Richland, WA, it was decided a short symposium (with printed proceedings) related to the objectives of the S-1041 project would enhance the annual meetings and further inform participants on topics related to the project's objectives. Eventually, these proceedings were to be posted on the S-1041 website. To this end, the first symposium was planned for the 2010 meeting at the Eastern Regional Research Center (ARS, USDA) and was to include speakers from the facility as well as the region surrounding the meeting.

Year	Symposium Title	Location
2010	Conversion Technologies for Biofuels	Eastern Regional Research Center, ARS, USDA, Wyndmoor, PA
2011	Where There's Smoke, There's Fuel: A Symposium on the Thermochemical Conversion of Biomass to Fuels	Advanced Technology and Research Center, Oklahoma State University
2012	The Science and Engineering for a Biobased Industry	National Institute of Food and Agriculture, USDA, Washington, DC
2013	none held	
2014	The Science and Engineering for a Biobased Industry	Southern Regional Research Center, ARS, USDA, New Orleans, LA
2015	Stakeholder Perspectives on the Bioeconomy	Ohio Agricultural Research and Development Center, Wooster, OH

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POSTER PRESENTATIONS

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INTENSIFIED DRYLAND CROPPING SYSTEMS FOR FOOD AND FUEL PRODUCTION

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Camelina has potential to substitute fallow period in the predominant wheat fallow (WW-FAL) cropping system in the Northern Great Plains. Production of biofuels on fallow land will benefit both farmers and environment without creating any "food versus fuel" crisis. In a multiyear field study (2008 to 2015), we evaluated the sustainability of replacing fallow with camelina in WW-FAL rotation with respect to agronomic, economic and energetic performance. We also examined how to improve the sustainability of camelina production via optimization of agronomic practices.

Replacing fallow with camelina resulted in 13.2% wheat yield penalty; whereas, 907 kg ha^{-1} of camelina was produced. Greater and annually biomass production thus enhancing soil organic matter, higher precipitation use efficiency and protecting soil against erosion in WW-CAM indicated more agronomic sustainability of this system. WW-CAM also outperformed WW-FAL by 30% greater net energy output and similar energy efficiency. Despite agronomic, energetic and ecological benefits, economic analysis revealed that at existing market prices and production costs, WW-FAL provides greater net returns to growers due to lower variable costs. We found there was potential to curb production costs of camelina through improving nitrogen fertilization use efficiency and reducing herbicide application. Besides lower production cost, higher grain price (the breakeven of \$0.358 kg^{-1}) and/or greater grain yield are essential to attract producers to plant camelina.

THERMODYNAMICS OF BIODERIVED CHEMICALS: IMPROVING ASSOCIATION MODELING

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Process streams encountered in the bioeconomy consist of polar solutions which hydrogen bond (associate). Such systems present difficulties in modeling phase equilibria because association causes large deviations from ideal behavior. Capital and time must be invested to model mixture phase behavior and this slows industrial implementation of biobased processes. Many models have been designed to account for association but they often utilize more parameters than can be determined with confidence of physical relevance.

Two main approaches for modeling hydrogen bonding are chemical theory (CT) and Wertheim's theory (WT). The former represents hydrogen bonding using equilibrium reaction parameters (Campbell, 1994). In contrast, WT is a statistical mechanics approach which develops the Helmholtz energy for interactions between attractive sites on repulsive cores (Wertheim, 1984, 1986). Both methods require accurate representation of the monomer fraction to calculate the governing key parameter for hydrogen bond formation, K (in CT) and Δ (in WT). This can be found microscopically, using spectroscopy together with molecular simulations, or macroscopically by fitting experimental vapor pressure data.

Binary systems, consisting of a self associating component in an inert solvent, were modeled by linearly combining combinatorial, association and residual terms. The combinatorial and residual terms were calculated using Flory's solution theory and nonrandom two fluid theory (NRTL), respectively. The association term was evaluated using both CT and WT and the results compared. Although derived from completely different equations, we proved the two approaches are numerically identical. The resulting model is applied to phase equilibria for alcohols in n-heptane.

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INVESTIGATING THE DRYING BEHAVIOR CHARACTERISTICS OF WOOD AND WOOD POLYMERS USING THERMOGRAVIMETRIC ANALYZER

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Thin layer drying of red oak wood components and wood polymers (cellulose and lignin) were carried out using a thermogravimetric analyzer (TGA) under isothermal condition at 105°C in nitrogen atmosphere. The weight, time, temperature data from TGA were processed to plot drying characteristics curves, which were used to explain differences in drying behavior. Data were used to calculate effective moisture diffusivity (D_{eff}). Focus was placed on the determination of the effective diffusivity of the materials (bark, sapwood and heartwood of red oak) in the falling rate drying period as well as comparative analysis. The (D_{eff}) values for bark, sapwood and heartwood were 3.74, 7.08 and 5.20 x 10^{-7} m^2/s, respectively. Sapwood had the highest (D_{eff}). The bark had the lowest (D_{eff}).

THE STUDY OF METHANE REFORMING WITH CARBON DIOXIDE OVER Ni BASED BIMODAL PORE CATALYST

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The dry reforming of methane (DRM) with CO_2 has been studied due to its important applications in producing of syngas ($CO + H_2$), removal of two greenhouse gases and upgrading of biogas (mainly composed of CH_2 and CO_2) into value added chemical (Alipour et al., 2014; Bao et al., 2013; Lu et al., 2012; Serrano-Lotina et al., 2014). Compared to the noble metal catalysts, the nickel based catalyst is suitable for industrial scaled up DRM due to its high activity and low cost. However, nickel based catalysts have been encountering a challenge that is the active metal sintering and coke deposition, leading to the catalyst deactivation and poor stability (Horvath et al., 2013; Li et al., 2014). It has been reported the deactivation of nickel catalysts can be suppressed by adding promoters like strong Lewis bases with the enhancement of chemisorb CO_2, such as MgO and CaO, and like lanthanide elements with the capacity of oxygen storage and release, such as CeO_2 and La_2O_3 (Chen et al., 2013). Aluminum oxide is a commonly applied catalyst carrier owing to its good pore size dispersion, high specific surface area and high mechanical strength.

We report the bimodal NiCeMgAl catalysts with different NiO loading were synthesized by the refluxed coprecipitation method and were evaluated for DRM catalytic performance. The sample containing 15 wt% NiO loading (Ni_{15}CeMgAl) was active at 750°C with a high CH_4 conversion of 96.5%. Ni_{15}CeMgAl catalyst kept its bimodal porosity after reduction and DRM reaction. The evolution of the Ni_{15}CeMgAl catalyst before and after the DRM reaction was investigated by BET, XRD, TEM and TGA techniques. A schema of the DRM reaction on the bimodal Ni_{15}CeMgAl catalyst was proposed and the correlation between the structure evolution and catalytic performance change is presented.

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TECHNOECONOMIC ANALYSIS OF BALED AND PELLETED CORN STOVER SUPPLY LOGISTICS FOR BIOFUELS PRODUCTION

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Corn stover feedstock supply logistics play a pivotal role in the overall sustainability of biofuels production; thus, it should be reliable and cost effective for uninterrupted operation of the corn stover based biorefineries. Over the years, different supply systems, specifically with and without central storage facilities (Hess et al., 2007; Hoefnagels et al., 2014; Miao et al., 2012; Searcy and Hess, 2010; Searcy et al., 2014; Shah, 2013), and biomass densification options, including bale, pellet and cube (Richard, 2010; Nguyen et al., 2014; Searcy et al., 2014; Argo et al., 2013), have been investigated. However, an economic corn stover supply method from field to biorefinery is not yet identified due to uncertainties associated with the process and data quality. In recent years, there have been successes with the pretreatment and ethanol fermentation of corn stover pellets without preprocessing, ie, milling, (Li et al., 2014; Guragain et al., 2013; Bals et al., 2014; Hoover et al., 2014; Ray et al., 2013), which opens up possibilities of including pellets as an integral part of the feedstock supply chain. The main objective was to assess the corn stover supply cost incorporating pellets and conventional bales. A model to supply feedstock for 30 million gal/yr cellulosic biofuels production was developed to integrate corn stover supply from field to preprocessing step at the biorefinery. While corn stover bales require a preprocessing step before pretreatment to break down bales into smaller particle sizes (ie, 4 to 6 mm (NREL, 2011)), pelleted corn stover (ie, 6.5 mm diameter and 44.5 mm thick (Theerarattananoon et al., 2012; Rijal et al., 2012)) may be supplied directly to pretreatment reactors without a preprocessing step; thus, integration of a preprocessing step provides a fair comparison to feedstock supply cost in the form of a bale and pellet. In addition to the two major forms of corn stover feedstock, two major scenarios considered during this research included: 1) corn stover bales first transported to the central storage facility in the form of bales, then either in form of bales or pellets to the biorefinery and 2) corn stover bales transported to biorefinery from field edge in the form of bales. A preprocessing step at the biorefinery was added for both of these major scenarios; however, pelleted corn stover also was analyzed without a preprocessing step at the biorefinery. An industrial scale corn stover feedstock supply data for conventional bales and literature based data for pellets were the main inputs to the models and are used to analyze mass and energy balance. Economic analysis, and sensitivity and risk analyses on unit corn stover supply cost were conducted. Outcomes will help cellulosic biorefineries evaluate the technoeconomic performances of alternative feedstock supply systems.

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EVAPORATOR FOULING TENDENCIES OF THIN STILLAGE AND CONCENTRATES FROM THE DRY GRIND PROCESS

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In the US, more than 90% of fuel ethanol production is from the dry grind process. More than 200 maize processing plants use multiple effect evaporators to remove water from thin stillage during dry grind. Evaporator fouling occurs during thin stillage concentration and may be from deposition of proteins, fat, fiber and/or carbohydrates on evaporator surfaces. The consequences of fouling include increased capital costs, operating costs and environmental footprint of cleaning chemical disposal. Despite chronic problems of evaporator fouling in the corn process industry, there have been relatively few studies to understand thin stillage fouling (Arora et al., 2010; Challa et al., 2015; Rausch et al., 2013; Singh et al., 1999; Wilkins et al., 2006a; Wilkins et al., 2006b). The objective was to investigate effects of total solids and compositional variation on evaporator fouling during thin stillage concentration.

Many ethanol plants recover post fermentation corn oil; therefore, the effects of oil recovery on evaporator fouling also were studied. In earlier literature, glycerol accumulation in processing streams from thin stillage recycling was observed; therefore, experiments were conducted to compare the fouling rates when glycerol was added to thin stillage. Thin stillage (7% solids) had lower fouling rates compared to evaporator concentrates (8 to 11% solids). Addition of post fermentation corn oil (0.5 to 1.0%) increased thin stillage fouling rates but at higher oil concentration (1.5% added), rates decreased. At 10% solids content in evaporator concentrates, oil recovery had no influence on fouling rates. Glycerol addition (1%) to thin stillage increased fouling rates.

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IN VITRO FERMENTATION OF XYLOOLIGOSACCHARIDES FROM *MISCANTHUS × GIGANTEUS*

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Miscanthus x giganteus (MxG) is a warm season perennial grass that has gained attention as a bioenergy crop; it is a leading candidate because it produces high biomass yields and has low input requirements (Lewandowski et al., 2000). Previously, we demonstrated xylooligosaccharides (XOS) can be produced through autohydrolysis and recovered by carbon adsorption followed by ethanol elution. There is a lack of information on the functionality of XOS from MxG and as a value added product for cellulosic ethanol. Our objective was to perform *in vitro* fermentation of MxG XOS with *Bifidobacterium* spp. and human fecal culture, to compare with commercial XOS products.

Highly purified MxG XOS were cultured with beneficial bacteria, *Bifidobacterium adolescentis* and *Bifidobacterium catenulatum*. Both *Bifidobacteria* were able to utilize MxG XOS as a carbon source for proliferation while *B. adolescentis* grew faster than *B. catenulatum* with specific growth rates of 0.69 to 0.33/h^{-1}. The substrate utilization was 84.1% by *B. adolescentis* and 76.9% by *B. catenulatum*. MxG XOS was cultured further with human fecal microbiota. Commercial XOS from Wako and pectin were used as comparisons. A pH decrease, from 7.1 to 5.0, was observed during 12 h of fermentation. Change in pH was similar for the MxG and Wako XOS cultures. MxG XOS produced 466.2 mg/g acetic acid, 74.6 mg/g propionic acid and 84.2 mg/g butyric acid; total short chain fatty acids were highest among the substrates. The beneficial bacteria *Bifidobacterium* spp. and *Lactobacillus* spp. population increased during the fermentation of MxG XOS. Compared with Wako XOS, MxG XOS had similar *Bifidobacterium* spp., *Lactobacillus* spp., *Escherichia coli* and *Clostridium perfringens* cell titers. We substantiated MxG XOS as a prebiotic candidate could be utilized by *Bifidobacterium* spp. and fecal microbiota, be converted into beneficial metabolites and stimulate probiotics growth.

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VALUE ADDED CONVERSION OF WASTE COOKING OIL AND USED PET BOTTLES FROM CAMPUS WASTE INTO BIODIESEL AND POLYURETHANE FOAMS

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An innovative process for value added utilization of campus wastes, especially waste cooking oil and polyethylene terephthalate (PET) bottles, was developed and validated. Waste cooking oil collected from campus cafeterias was converted into biodiesel, which can be used as fuel for farm tractors and/or school buses. During the preparation of biodiesel from waste cooking oil, crude glycerol was generated as a byproduct, which was then incorporated into the glycolysis process of used PET bottles for the production of polyols and polyurethane (PU) foams. The effect of the crude glycerol to PET ratio on the properties of polyols and PU foams was explored. A mass balance for biodiesel and PU foam production from waste cooking oil and used PET bottles was obtained.

SWEETGUM BARK: GOOD AND BAD NEWS AS A BIOREFINERY FEEDSTOCK

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Liquidambar styraciflua L., also known as sweetgum, is a hardwood tree that grows voluntarily as understory in southeastern US pine forests. In addition to its timber and ornamental value, sweetgum could be used as biorefinery feedstock. Djioleu et al. (2014) reported that up to 72% of total carbohydrate contained in sweetgum wood could be converted into fermentable sugar by a combination of dilute sulfuric acid pretreatment and cellulase enzymatic hydrolysis. On the other hand, conversion of carbohydrate from sweetgum bark only yielded 50% of total fermentable sugars. Bark's low carbohydrate yield was due mainly to its severe resistance to cellulase hydrolysis. Although sweetgum bark is not an ideal material for saccharification, it contains valuable phytochemicals, such as shikimic acid (Martin et al., 2010). It was stipulated that sweetgum heartwood could be saccharified, while its bark could be extracted for valuable phytochemicals, adding value to the biorefinery and providing an efficient way to use all parts of the tree.

We investigated the antimicrobial and antiperoxidation potentials of water extracted sweetgum bark. Extraction was conducted with water in a Parr reactor set at 85°C and agitated at 144 RPM; biomass loading was 10% of the slurry; extraction lasted one hour. Total phenolics, expressed as gallic acid equivalents, contained in the liquid extract accounted for 12% of the total solid content. At a reconstituted concentration of 150 g/L, sweetgum bark water extract inhibited the growth of *Staphylococcus aureus* in a zone of 15 mm of diameter, as determined by the disc diffusion assay. Furthermore, the sweetgum bark water extract reconstituted at 16 g/L of solid inhibited lipid peroxidation of low density human lipoprotein (LDL) in the Thiobarbituric Acid Reactive Substance (TBARS) assay using copper induced oxidation. Sweetgum bark water extract contained antimicrobial and antiperoxidation phytochemicals. On the other hand, when reconstituted at a solid concentration of 4 g/L, the liquid extract inhibited cellulase activity by 50%, confirming that the bark is not ideal for saccharification.

In a biorefinery setting, sweetgum heartwood could be saccharified, while sweetgum bark could be exploited for its phytochemicals and its energy value, but not for its carbohydrates. The possibility of extracting valuable compounds with water, as opposed to using organic solvents, would allow for exhausted bark to be combusted safely after the extraction step.

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DILUTE ACID PRETREATMENT: INVESTIGATION OF ACID CONCENTRATION, TIME, TEMPERATURE AND SOLID TO LIQUID RATIO ON TOTAL SUGAR RELEASE FROM NAPIER GRASS

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Lignocellulosic biomass has gained much attention in the biofuel industry due to its promising characteristics of being a dedicated energy crop, requiring comparatively less water, nutrients, land, and not competing directly with food resources (Ghatak, 2011). Lignocellulosic biomass is composed of cellulose and hemicellulose, which are interlocking sugar polymers. These polymers are covered in a protective lignin matrix which helps prevent the decomposition of the sugar polymers (Hendriks and Zeeman, 2009). Due to its complex structure and recalcitrant nature often it is necessary to perform pretreatment on lignocellulosic biomass to break apart the structure and create sugar monomers (Yang and Wyman, 2008). Sugar monomers are precursors to many types of biofuels and biobased products; therefore, it is important to maximize the sugar recovery from biomass to improve efficiency and reduce operating costs of the conversion process. There are many proposed strategies for pretreatment (eg, physical, chemical, biological and hybrid); however, only a few remain technoeconomically feasible for scale up and commercialization. Dilute acid pretreatment of biomass was explored using Napier grass (*Pennisetum purpureum*). The factors of sulfuric acid concentration (2.50, 3.75 and 5.00% w/v), reaction time (45 and 75 min), temperature (120 and 130°C), and solid to liquid ratio (1:3, 1:6 and 1:9 part biomass to part dilute acid) were investigated in a split plot experimental design. After pretreatment, the remaining fibers were saccharified via cellulase enzymes for 72 hr at 200 RPM and 50°C to remove remaining sugars. Total sugar release was quantified by HPLC. An in depth understanding on how these factors and their interactions, if any, influence the release of sugar during the dilute acid pretreatment process is necessary for the optimization and overall efficiency of the conversion of biomass to biofuels.

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LIGNIN TO LIQUID FUELS AND VALUE ADDED PRODUCTS USING FAST PYROLYSIS AND ELECTROCATALYTIC UPGRADING

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Biomass fast pyrolysis (BFP), which uses heat (400 to 600°C) in the absence of oxygen to convert biomass to bio-oil, biochar and combustible gas, offers an alternative to fossil fuels and a means to alleviate the environmental impact of burning fossil fuels for energy production. The major product, bio-oil, can be upgraded to liquid hydrocarbon fuels, while biochar can serve as a solid fuel or soil amendment. The combustible gas coproduct typically is burned for needed process heat. However, the most valuable of the pyrolysis products, bio-oil is highly oxygenated, corrosive, low in energy content and unstable during storage due to the hundreds of compounds that make up bio-oil. As a means of improving bio-oil properties, electrocatalytic hydrogenation (ECH) is employed to reduce and deoxygenate reactive compounds.

We focused on the electrocatalytic stabilization of compounds derived from the pyrolytic depolymerization of lignin. As lignin is a component of biomass comprising up to 30% of the mass and 40% of the energy stored in biomass it offers potential as feedstock for BFP. Lignin model compounds representative of bio-oil components were subjected to ECH under mild conditions (80°C and 1 atm) using ruthenium on activated carbon (Ru/ACC) as a catalytic cathode. To date, model monomers (guaiacol, syringol, syringaldehyde, vanillin, p-cresol, creosol, eugenol etc) have been reduced to simpler compounds such as cyclohexanol and phenol, which have better heating values when compared to the starting substrates. Using this method, lignin derived model dimers such as 4-pehnoxyphenol also have been cleaved and reduced to cyclohexanol and phenol.

ALKALINE ORGANIC SOLVENT PRETREATMENT FOR 2,3-BUTANEDIOL PRODUCTION FROM DIVERSE BIOMASS RESOURCES

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Efficient pretreatment method to maximize sugars yield from biomass with minimum undesirable degradation of biopolymers is vital for lignocellulosic based biorefineries. Organosolv pretreatment is an effective method to improve enzymatic hydrolysis efficiency of pretreated biomass for biofuels and chemicals production. It also produces quality lignin for high value application. Acid catalyst commonly is used in organosolv pretreatment process, but it leads to loss of hemicellulose during pretreatment. Alkali catalyst is a promising approach for biomass pretreatment without sugar loss. However, vast variation in composition and structure of biopolymers among biomass types deters the optimization of a single pretretreatment method. All bioenergy resources, therefore, must be optimized separately to select the best pretreatment solvent for each type of biomass.

Pretreatments of grass (corn stover), hardwood (poplar) and softwood (douglas fir) were evaluated using various alkaline organic solvents, including dimethyl sulfoxide (DMSO), 2,3-butanediol, glycerol, ethanol, isopropanol and butanol. The results were compared with conventional aqueous alkali pretreatment. 0.4% alkaline (sodium hydroxide) alcohols and glycerol were promising for grass and hardwood, respectively. Pretreatment of softwood was not effective with these solvents, including 10% (w/v) aqueous sodium hydroxide. The quality of biomass derived sugars for 2,3-butanediol production using robust microbial cultures, such as *Bacillus licheniformis,* was equal to that of synthetic sugars. Research is ongoing to develop novel pretreatment approaches for softwood and characterization of biomass lignin using GC-MS and NMR.

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INHIBITORY EFFECT OF CELLOBIONIC ACID ON CELLOBIOHYDROLASE AND CELLOBIOSE DEHYDROGENASE

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The development of microbial fermentation platforms for the production of organic acids has gained interest in the last decade due to the reliability and cost effectiveness of such processes. In recent years, carboxylic acids have emerged as specialty acids due to their unique physiochemical properties. Cellulosic biomass, which is available at low cost and in widespread abundance, is a potential substrate for the bioproduction of carboxylic acids. We engineered *Neurospora crassa* for the production of cellobionic acid (CBA) directly from cellulose with exogenous laccase and redox mediator addition. In this system, cellulases convert cellulose to cellobiose, cellobiose dehydrogenase (CDH) oxidizes cellobiose to CBA and CDH is regenerated continuously by laccase and a redox mediator. While inhibition of cellulases by cellobiose has been studied extensively, cellobionic acid inhibition of cellulases has not received much attention, despite the discovery that oxidative enzymes produced by cellulolytic organisms generate aldonic acids from cellulosic substrates. We investigated the inhibition of cellobiohydrolase I by cellobiose and CBA using p-nitrophenyl-β-D-lactopyranoside as a model cellulosic substrate. Additionally, CBA inhibition of CDH was evaluated. The kinetic properties and mechanism of CBA inhibition were studied and compared to that of cellobiose inhibition.

TECHNOECONOMIC ANALYSIS OF BIODIESEL AND ETHANOL COPRODUCTION FROM LIPID PRODUCING SUGARCANE

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Biodiesel production from vegetable oils has increased progressively over the past two decades. However, due to the low amounts of oil produced per hectare from temperate oilseed crops (eg, soybean and canola), the opportunities for further increasing biodiesel production are limited. Genetically modified lipid producing sugarcane (lipid cane) possesses potential for producing biodiesel as an alternative feedstock because of sugarcane's higher productivity compared with soybean. Technoeconomic models were developed for biodiesel and ethanol coproduction from lipid cane, assuming 2, 5, 10 and 20% lipid concentrations in the harvested stem (dry mass basis).

The models were compared with a conventional soybean biodiesel process model to assess lipid cane's competiveness. In the lipid cane process model, the extracted lipids were used to produce biodiesel by transesterification and the remaining sugar was used to produce ethanol by fermentation. The biodiesel production cost from lipid cane decreased from $0.86 to 0.59/L as the lipid content increased from 2 to 20%; this cost was lower than obtained for soybeans ($1.08/L). The ethanol production costs from lipid cane were between $0.39 and 0.45/L. The internal rate of return (IRR) for the soybean biodiesel process was 15.0% and the IRR for the lipid cane process went from 14.6 to 24.0% as the lipid content increased from 2 to 20%. Because of its high productivity, lipid cane with 20% lipid content can produce 6,700 L of biodiesel from each hectare of land; whereas, soybean can only produce approximately 500 L of biodiesel from each hectare of land.

TECHNOECONOMIC ANALYSIS OF ETHANOL PRODUCTION FROM TEMPERATE × TROPICAL MAIZE

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Temperate × tropical maize (TTM) is a maize hybrid (*Zea mays* L.) which was bred by crossing temperate and tropical parents for sugar and biofuel production. TTM has a prolonged vegetative growth and accumulates soluble sugar in the stalk which provides an opportunity to emulate the sugarcane ethanol industry in Brazil. Soluble sugars (sucrose, glucose and fructose) accumulate in the TTM stalk during maize development and the concentration could increase up to 30% (w/w) of dry material (Chen et al., 2014). Biomass yield of TTM can reach 8.0 tons per acre (dry basis). Technoeconomic models were developed to evaluate the economic feasibility of TTM for ethanol production.

In the TTM process models, soluble sugars were extracted and fermented to produce ethanol. Bagasse, a byproduct in the TTM process, was burned to produce steam to generate electricity for the TTM processing plants, with the excess sold to the grid. Process model was built using SuperPro Designer software, which quantifies the processing characteristics, energy requirements, material flows and conversion efficiencies at each step. Ethanol production costs from TTM were between $1.70 and 2.09/gal, depending on the composition of TTM. Ethanol yield from TTM was 345 gallons per acre of land area, when TTM was harvested at R5 growth stage. Sensitivity analyses will be conducted to determine variations of the ethanol production cost with the variables used in the economic analysis.

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REINFORCEMENT OF POLYLACTIC ACID USING PYRENE FUNCTIONALIZED MULTIWALLED CARBON NANOTUBES

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There is a growing need for biodegradable, biocompatible, ecofriendly biopolymers to replace the increasingly used conventional petroleum polymers. However, mechanical strength and thermal stability of biopolymers must be enhanced to replace the petroleum based polymers. We investigated a new method of functionalizing the multiwalled carbon nanotubes (MWNT) used as reinforcement to improve the bonding with polylactic acid (PLA) using π-π stacking method. Composites were prepared by varying the concentration of the filler material (0, 1, 3, 5 and 7 wt%). Tensile strength and modulus were determined using Instron tensile testing machine, morphological characteristics using scanning electron microscopy (SEM), thermal stability using the thermogravimetric analyzer (TGA) and chemical bonding between the matrix and filler material was studied using Fourier transform infrared spectroscopy (FTIR).

The composite prepared with 5 wt% MWNT exhibited the maximum tensile strength and modulus with increases of 74.17 and 117.5%, respectively, when compared to 100% PLA. As seen in SEM images, functionalized MWNTs were dispersed homogenously and free from agglomerations as compared to the composite prepared using nonfunctionalized MWNTs. The formation of MWNT–NH-CO-PLA bonds was confirmed using FTIR. Onset and oxidation temperatures of the composites increased progressively with the increase in MWNT and were maximum for 7 wt% MWNT at 292˚C and 435.5˚C, respectively.

THE ECONOMICS OF BIOMASS BASED CHEMICALS

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We assessed the economic viability and environmental impacts of substituting petrochemicals with biomass based chemicals. While using a mathematical model, we simulated a biorefinery that produced polylactic acid (PLA) and compared the economic outcome with that of a biorefinery that converted biomass to biogas. Using cost benefit analysis, we calculated the net economic benefits of the bioenergy production systems and identified key parameters that hinder (facilitate) the development of the biomass based chemical industry. Higher natural gas and CNG prices, lower PLA prices and less efficient PLA technologies resulted in barriers to the commercialization of the biomass based chemicals industry yet increased the relative advantage of biogas production and conversion to CNG. While regions that experience relatively low natural gas prices (eg, Pennsylvania and Ohio) may benefit from the commercialization of a biomass to PLA, others may prefer more production of waste to biogas and CNG (eg, the Northeast, including Maine and Vermont). We also identified the breakeven values of key parameters that resulted in PLA production being economically viable.

PRODUCTION OF BIOBASED POLYCARBONATE POLYOLS FROM CORN ETHANOL COPRODUCTS FOR POLYURETHANE APPLICATIONS

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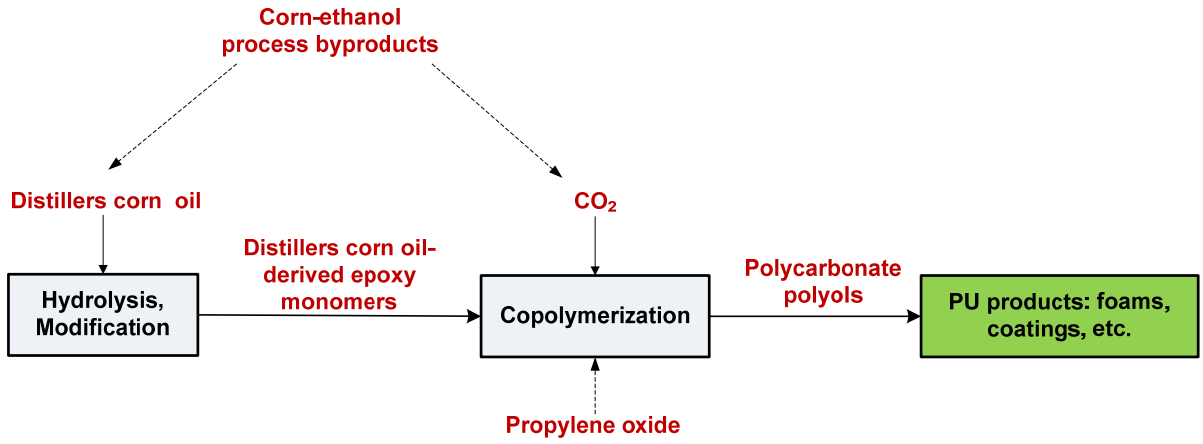
Distillers dried grains with solubles (DDGS) and CO_2 are two major fermentation coproducts of the corn ethanol process. In recent years, crude corn oils (also called distillers corn oil) have been extracted from DDGS to improve the economics of the corn ethanol process. An innovative technology is proposed to synthesize biobased polycarbonate polyols from CO_2 and distillers corn oil for the production of polyurethane (PU) products. The proposed technology provides a novel and environmentally preferable alternative to petroleum based polyols for PU applications and effectively incorporates CO_2 into polyol chains. This technology will benefit corn producers and corn ethanol plants via value added conversion of their coproducts to valuable biobased polyols and PUs and also will help reduce the carbon footprint and improve the sustainability of ethanol production.

Key challenges addressed were:

1) Effective conversion of distillers corn oils to polycarbonate polyols: functionalized epoxy monomers will be prepared from crude corn oils via saponification followed by epoxidation with epichlorohydrin, based on optimized conditions.
2) Catalytic polymerization of distillers corn oil derived epoxy monomers and CO_2: catalyst screening and the development of new catalysts will be conducted for producing polycarbonate polyols from distillers corn oil derived epoxy monomers via incorporation of CO_2 for PU applications.



BIOLOGICAL CONVERSION OF GREENHOUSE GASES (CH_4 AND CO_2) TO METHANOL

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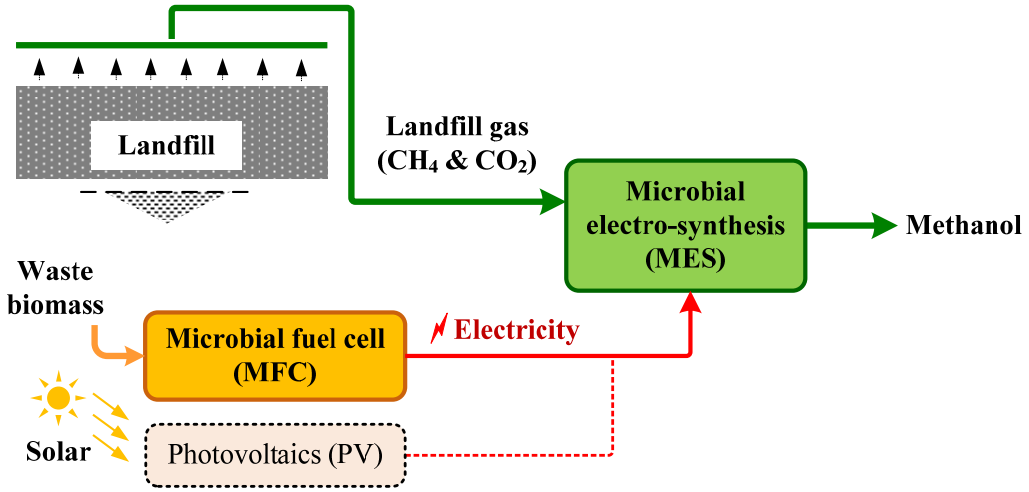
Landfill gas, which contains mainly CH_4 and CO_2, is one major source of greenhouse gas emissions in the US. A promising approach to reduce these emissions is to convert landfill gas into methanol, which is a liquid fuel and a valuable precursor for other fuels and chemicals. However, current CH_4 and/or CO_2 to methanol technologies are economically unfeasible due to high costs for energy and chemical inputs. We propose to develop an innovative landfill gas to methanol conversion system that is based on advanced technologies in fields of microbiology and electrochemistry. The project, if successful, will improve the energy security and societal sustainability of the US by reducing consumption of fossil fuels and imports of energy from foreign sources and by reducing greenhouse gas emissions.

Key challenges addressed were:

1) Current methane to methanol conversion technologies require expensive landfill gas purification processes due to toxicity of impurity gases (H_2S and NH_3) in landfill gas. We will address this issue by isolation and utilization of H_2S/NH_3 tolerant bacteria which can produce high yields of methanol from the methane in landfill gas.
2) Expensive chemicals, such as formic acid, currently are used for methanol accumulation by bacteria, but are economically unfeasible. Based on the isolated H_2S/NH_3 tolerant bacteria, we will further develop a bacterium that can convert landfill gas into methanol without using costly chemicals.



ENGINEERING *NEUROSPORA CRASSA* FOR CELLOBIONATE PRODUCTION FROM CELLULOSIC BIOMASS

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In recent years, carboxylic acids, such as lactobionic acid (LBA) have emerged as specialty acids due to their unique physiochemical properties. They are high value added organic acids, with numerous applications that span the pharmaceutical, food and cosmetics industries. Its sister chemical cellobionic acid (CBA) is expected to have similar applications. To compete with petroleum based processes for the production of carboxylic acids, the development of microbial processes utilizing low cost substrates is essential. LBA currently is produced through chemical synthesis in an energy intensive process requiring costly metal catalysts. Alternatively, LBA or CBA can be produced biologically by various bacterial and fungal strains using refined sugars as the substrate. Cellulosic biomass, which is available at low cost and in widespread abundance, is a potential alternative substrate for the bioproduction of carboxylic acids. We report engineering *Neurospora crassa* strain for the production of CBA, directly from cellulose with exogenous laccase and redox mediator addition.

We report the production of cellobionic acid (cellobionate) directly from cellulosic biomass by a genetically engineered fungus strain *Neurospora crassa*. After deleting nine genes essential for cellobiose and cellobionate utilization and over expressing laccase gene from *Botrytis aclada*, the engineered strain is able to convert pretreated poplar to cellobionate at high yield without addition of exogenous enzymes.

DEVELOPMENT OF A PHASE CHANGE MATERIAL FROM FATTY ACID METHYL ESTERS FOR REDUCING ICE ON CONCRETE PAVEMENTS

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Phase change materials (PCMs) are used as an effective way of storing thermal energy. Thermal energy is absorbed/released when PCMs undergo a phase change. Incorporating PCMs into concrete in airport runways has been suggested as a means of preventing surface ice formation on runways. We report on the experimental development of a PCM from mixtures of fatty acid methyl esters (FAMEs) providing solid-liquid transition behaviors near 0°C with a high enthalpy of fusion. The phase behavior of FAME mixtures was dependent on the composition and molecular properties of the FAME. The phase behavior of binary mixtures of medium length saturated FAME, methyl laurate and methyl myristate, demonstrated ideal properties for PCMs. The developed mixture has the properties necessary to be a high performance PCM with the potential to reduce the levels of icing on concrete pavements.

IMPROVING ALGAL BIOMASS YIELDS BY GROWING ALGAE ON MIXED FOOD PROCESSING WASTEWATERS

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Cultivating algae on food processing wastewater is a cheap and efficient way to both produce biomass and prevent environmental pollution. However, due to the imbalanced nutrient profile in wastewater, biomass yields of algae grown on dairy wastewater and meat processing wastewater were low (Woertz et al., 2009). Although developed methods, such as aeration and acid digestion, could improve biomass yield, they also made the wastewater treatment process complex and improved the cost (Mata, 2012). We improved the biomass yield of algae grown on dairy wastewater and meat processing wastewater by mixing different wastewaters.

Based on nutrient profile analysis, we hypothesized the lack of certain nutrients in some meat processing wastewater was the bottleneck. After testing algae growth on individual wastewaters, we used the best one as base and mixed it with others; biomass yield reached 0.675 to 1.538 g/L, which was higher than the averaged sum of any two wastewaters, suggesting synergetic effects. Furthermore, ammonium and total nitrogen removal rates in mixed meat processing wastewater were improved to 68.75 to 90.38 and 30.06 to 50.94%, respectively.

The lack of ammonium was the main reason for low biomass yield of algae grown on dairy wastewater. The meat processing wastewater from slaughtering process was mixed with dairy wastewater to improve the ammonium content. On three types of mixed wastewater, mother liquor, salt whey and liquid whey, biomass yields of algae reached 2.66, 1.32 and 2.00 g/L, respectively, which were 129.31, 26.52 and 110.53%, higher than on nonmixed dairy wastewater. In comparison with nonmixed wastewater, contents of phosphorous and chemical oxygen demand left in mixed wastewater, after algae cultivation, were reduced. The strategy based on mixing wastewaters developed in this work is a simple way to balance nutrient profile of wastewater and improve biomass yield of algae and nutrient removal.

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DRY REFORMING OF METHANE TO SYNTHESIS GAS OVER TUNGSTEN CARBIDE NANOPARTICLES IN BIOCHAR MATRIX

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Biogas from landfill sources is composed of 45 to 55% CH_4, 30 to 40% CO_2 and 5 to 15% N_2; biogas from organic waste anaerobic digesters contains 55 to 65% CH_4, 35 to 45% CO_2 and 1% N_2. Biogas, as a natural gas substitute, is used widely and primarily in industry for burning in a boiler or in a stove to obtain heat or for supplying to a gas engine for electricity generation. The use of biogas is as internal combustion engine (ICE) fuel but the high CO_2 concentration decreases its energy value and limits engine peak power. Furthermore, unstable engine performance and high CH_4 concentrations in the exhaust will arise when engine loads are low. Efforts have been performed to remove CO_2 from biogas before it is used as the ICE fuel; however, this practice may increase the process cost and decrease its availability in power generation and transportation. Biogas has been studied for production of hydrogen as fuel cell feedstock; however, a high level of purity is required which makes the process unprofitable. Another promising approach is biogas reforming to syngas, followed by generating liquid hydrocarbons through Fischer–Tropsch synthesis (FTS). Currently, in industry, syngas is made from natural gas or coal; neither is renewable/sustainable feedstock. CH_4 and CO_2 are the main components of biogas, although both have been identified as the most important greenhouse gases. Also, they are key reactants for dry reforming process. Therefore, the dry reforming of methane process for syngas production reaction is a route to reduce greenhouse gas emissions.

Our objective was to demonstrate the feasibility of using biochar as a raw material for tungsten carbides (WC) nanoparticles synthesis through a carbothermal reduction (CR) method. Tungsten carbide nanoparticles were characterized for physicochemical properties by multiple morphological and structural methods (eg, SEM, TEM and XRD). Characterization results revealed the transformation of tungsten oxide (WO_3) to tungsten carbide nanoparticles involved the following sequence steps: $WO_3 \rightarrow WO_2 \rightarrow W \rightarrow W_2C \rightarrow WC$. The lower the reaction temperature, the lower the CH_4 and CO_2 conversions as well as the lower CO yield since dry reforming is an endothermic reaction. CH_4 conversion was observed to decrease with an increasing of CH_4/CO_2 ratio; whereas, CO_2 conversion increased with the increasing of CH_4/CO_2 ratio. The higher the GHSV, the lower the CH_4 and CO_2 conversions as well as the lower the CO yield. The stability testing of the tungsten carbide nanoparticles in biochar matrix showed no catalyst deactivation during the 500 h test duration.

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COMPARISON OF ENVIRONMENTAL AND ECONOMIC IMPACTS OF LOGISTICS FOR OHIO GROWN SOYBEAN EXPORTED TO CHINA

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Almost half of the 6.7 million tons of soybean grown in Ohio are exported and a major share of it is exported to China (Informa, 2012). The annual economic impact of $5.3 billion from soybean production emphasizes the importance in Ohio. Agricultural commodities are transported across the US and exported overseas using different transportation modes, namely truck, railroad, barges and ocean shipments. Soybeans from Ohio usually are exported via the Central Gulf or the Atlantic ports (Informa, 2012). Recent rapid expansion of the Western railroad systems has opened up a viable alternative for soybean supply chain in the future as the west coast is closer to the Asian markets. Thus, the main objective of this study was to analyze the environmental and economic impacts of the transportation of soybeans harvested in Ohio farms to the nearby rail or barge using trucks, then using rail or barge to the export ports where they are exported via cargo ships. We compared the environmental impacts using life cycle analysis (LCA) tools and costs associated with the logistics of exporting Ohio grown soybeans from farms to a port in China via the Atlantic, Gulf and the Pacific ports of the US. Modeling of logistics flow options and their environmental impacts was performed using LCA software. Models to compare the economics of each mode of transportation for different logistics flow options also were developed. The environmental and economic metrics are, respectively, compared in terms of total CO_2 equivalent emissions and dollars per metric ton soybeans delivered to the exported port. This comparison of the environmental and economic impacts of the logistics would help choose the best alternative of the existing options and could help contribute for a more sustainable supply chain for soybeans as well as other agricultural commodities exported from Ohio and its neighboring states.

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BIO-OIL OPTIMIZATION FOR A CONTINUOUS FLOW HYDROTHERMAL LIQUEFACTION REACTOR

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Hydrothermal liquefaction (HTL) is a novel and promising technology for producing renewable fuels. During this process biomass, mainly algae, is subject to high temperatures, 250 to 400°C and pressures, 5 to 25MPa (Toor et al., 2011). If the biomass remains under these conditions for sufficient time, four different products are achieved; gas, aqueous phase extracts, bio-oil and residual solids (López Barreiro et al., 2013). Bio-oil is the most desirable product because of the similarity to crude oil, resulting in a usability as a liquid fuel (Ross et al., 2010).

Recent studies involving batch experiments by Valdez et al (2014) have led to the formulation of a kinetic model for HTL consisting of six equations. The components accounted for are: protein, lipid, carbohydrate, aqueous products, bio-oil and gas. While the model has been validated for batch experiments, it has not been validated for a continuous system, which has been shown to require lower residence times when compared to batch experiments (Toor et al., 2011; Elliott et al., 2014). Our aim was to design and build a continuous flow system to test the validity of the kinetic model in the context of continuous flow reactors.

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BINDER COMPOSITION AND INTERMEDIATE TEMPERATURE CRACKING PERFORMANCE OF ASPHALT MIXTURES CONTAINING RECYCLED ASPHALT SHINGLES

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The use of recycled asphalt shingle (RAS) as a partial replacement for petroleum based virgin asphalt binder has received considerable attention in recent years (Elseifi, 2012). The objective of this study was to conduct a comprehensive laboratory evaluation of the composition of asphalt mixtures containing RAS including stone mastic asphalt. Laboratory testing evaluated molecular composition using gel permeation chromatography and the extent of aging from Fourier transform infrared spectroscopy data (Negulescu et al, 2006). High concentrations of high molecular weight RAS asphaltenes decreased the fracture resistance of the asphalt mixtures. The use of rejuvenating agents did not reduce the concentration of the highly associated asphaltenes and thus they failed to improve the cracking resistance of the modified mixes.

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OXIDATION REDUCTION POTENTIAL (ORP)-BASED MICRO-AERATION SYSTEM FOR ANAEROBIC DIGESTION

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Anaerobic digestion (AD) technology has promise for recovering energy from waste materials, eg, food wastes, agricultural residues and energy crops. The AD process is susceptible to process failures due to accumulation of short chain organic acids known as volatile fatty acids (VFAs).

Microaeration in AD processes could promote the diversification of bacterial communities without affecting the activity of methanogens (Lim et al., 2014). In our research, an oxidation reduction potential (ORP) based microaeration system was proposed as a process control strategy to reduce excess VFAs. The performance of an AD reactor semicontinuously fed with Napier grass (*Pennisetum purpureum*) was compared between anaerobic and microaeration conditions. Methane yields and total VFAs to alkalinity ratios were used as the main indicators of reactor performance. The automatic microaeration system could be controlled precisely based on ORP level. Further investigation will be conducted to evaluate the effect of micro-aeration on controlling VFA build up in AD systems.

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ACTIVATED CARBONS FROM HERBACEOUS BIOENERGY CROPS

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During the last decade, government has invested resources in planting various types of bioenergy crops in the northeastern region with an intent to supply ample feedstock to future cellulosic ethanol plants. With no cellulosic ethanol plant in the near future, all the harvested crops currently are used for heating purposes, which can serve as a demotivating factor for landowners. However, there exists potential to convert these crops into activated carbon, which currently sells at $42/kg.

Activated carbon is a widely used adsorbent in wastewater and flue gas treatments and in electrochemical applications. Therefore, the aim of our research was to evaluate production potential of activated carbons from two bioenergy crops (*Miscanthus* and switchgrass) currently grown on reclaimed mine lands in West Virginia. Pyrolysis has been performed to produce biochars, bio-oil and gaseous products. Biochars were activated chemically using three chemical agents, KOH, K_2CO_3 and H3PO4, at 900°C. Resulting activated carbons are being tested for porosity, pore size distribution, pore structure, surface area and adsorption properties.

IMPACT OF LIGNIN COMPOSITION ON LIGNIN DROPLET SIZE DURING DILUTE ACID PRETREATMENT

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Lignocellulosic biomass has potential as a renewable resource for global energy and production of biomaterials. Biomass consists of three main polymers, cellulose, hemicellulose and lignin. Cellulose is a homopolymer of glucose while hemicellulose and lignin are heteropolymers. Lignin is made of syringyl (S), guiacayl (G) and p-hydroxyphenyl (H) units. Pretreatment of biomass is a critical step to open the biomass structure and reduce its recalcitrance to enzymatic hydrolysis. Several investigators have demonstrated the S/G ratio of lignin has an effect on pretreatment effectiveness. Lignin is known to solubilize, redistribute, precipitate and coalesce as droplets during conventional pretreatment processes (Li et al., 2014). These transformations vary based on the type of the pretreatment process and are attributed to differences in the chemical composition and distribution of lignin in biomass. These transformations vary based on the type of the pretreatment process and are attributed to differences in chemical composition and distribution of lignin in biomass. Lignin can inhibit enzymatic cellulose hydrolysis by creating a physical barrier to enzymes and through lignin-enzyme interactions (Berlin et al., 2005). A higher S/G ratio content of lignin, as well as a higher percent of lignin contained in the biomass, can lower the theoretical yield in the saccharification process (Guo et al., 2009). Droplet size was found to vary by pretreatment conditions when using isolated organosolv lignin from corn stover (Selig et al., 2007). Several scientists have observed lignin droplets using one biomass, such as corn stover (Donohoe et al., 2008; Selig et al., 2007) or wheat straw (Zeng et al., 2013). t is necessary to fill gaps in the current research to see how S/G ratios of lignin affect droplet size and area. This information could lead to further understanding of how enzymatic hydrolysis yields and rates are affected by the lignin under dilute acid process conditions. The goal of this project was to delineate differences in the distribution of lignin droplets after dilute acid pretreatment in order to understand how the S/G ratios of lignin affect enzymatic hydrolysis.

Three biomass samples, bagasse, wheat straw and poplar, with known chemical composition were acquired from National Institute of Standards and Technology, US Department of Commerce. Lignin S/G ratios were in the range of 0.50 to 0.69 for wheat straw, 0.83 to 1.4 for bagasse and 1.3 to 2.0 for poplars (Lopes et al., 2011; Rahikainen et al., 2013; Sannigrahi et al., 2010; Zeng et al., 2013). A one step aqueous ethanol organosolv procedure without presoaking (Wildschut et al., 2013) was used to obtain lignin from biomass samples. Isolated

lignins with different S/G ratios and pure cellulose filter paper were subjected to dilute acid pretreatments (0.75% w/w sulfuric acid) at 120, 150 and 180ºC. Subsequently experiments were performed with whole biomass at the same conditions. Imaging of the pretreated filter paper was done using scanning electron microscopy (SEM) to observe visually and quantify the distribution of lignin droplets.

Differences in the lignin distribution using pure cellulose and isolated lignin at each pretreatment temperature is depicted in Fig. 1. A mix of large and small droplets that increase in amount as temperature increases in Series A. Series B has very small droplets covering the cellulose throughout at each temperature. Series C has large and small droplets that are more uniform in size than in Series A. Series C also has an increasing amount of droplets with increasing temperature. As seen in Fig. 1, the A series of images depicts wheat straw at temperatures of 120 (A-1), 150 (A-2), and 180ºC (A-3). Of the biomass in this study, wheat straw had the smallest S/G ratio range of 0.50 to 0.69 and the smallest mass fraction of total lignin at 18.1%. There were a greater amount of droplets at the highest temperature, as well as a mix of larger droplets. Wheat straw, at 180ºC, had a mix of many small to very large droplets in the image shown at 10,000x magnification in A-3. The larger droplets had diameters up to 5.0 μm while the smallest was below 0.10 μm. Sugarcane bagasse isolated lignin after pretreatment with pure cellulose is shown in Fig. 1, Series B. The droplet size at 10,000x magnification was small with many at and below 0.10 μm diameter. The largest droplet in Fig. 5, B-2, was 0.80 μm in diameter. The S/G ratio range was in the middle for bagasse, at 0.83 to 1.4. Bagasse also had the medium amount of total lignin. In Fig. 1, Series C, poplar showed droplets sized from 5 to less than 0.10 μm in diameter. Image C-3 of poplar, pretreated at 180ºC, had many droplets of similar sizes in the realm of 0.5 μm in diameter. Poplar had the highest S/G ratio range of 1.3 to 2.0 and highest lignin of 27.2%.

In Fig. 2, the pretreated whole biomass was compared in the same way as the pure cellulose from Fig. 1. Wheat straw, with many small droplets covering the biomass at each temperature, is shown in Series D. There were variations in large and small droplets similar to the pure cellulose (from Series A). Series E is bagasse with many tiny droplets at each temperature and some larger droplets at 180ºC. Again, similarities in droplet sizes between Series E and Series B can also be seen. The droplets of Series F, poplar, appeared larger at each temperature. Just as in the other Series, F and C had similar droplet distribution and size.

There was a visual trend in droplet amount and size among the pretreated pure cellulose and isolated lignin samples. Wheat straw was observed to produce many large and small droplets of different sizes with an increase relative to higher temperatures. Bagasse was coated in a layer of tiny droplets that gave the surface a textured appearance throughout each temperature. Mostly uniform small and large droplets formed on poplar with an increase in amount as temperature increased. Variability in droplet morphology was observed for each case.

Differences observed between lignin droplet behaviors in the whole biomass were due to the complex nature of lignin extrusion from within the cellular structure and location of lignin within the biomass. At the start of this study, it was expected that a higher S lignin content and larger percent of lignin, would form more droplets on the cellulose. This was not the case, as poplar had the highest amount of lignin and highest S/G ratio. Even though poplar did have a

large amount of droplets, bagasse and wheat straw also developed many that coated the cell walls. Larger droplet size did not correlate to a greater amount of lignin or S/G ratio; however, lignin droplets appeared to increase in amount as temperatures increased.

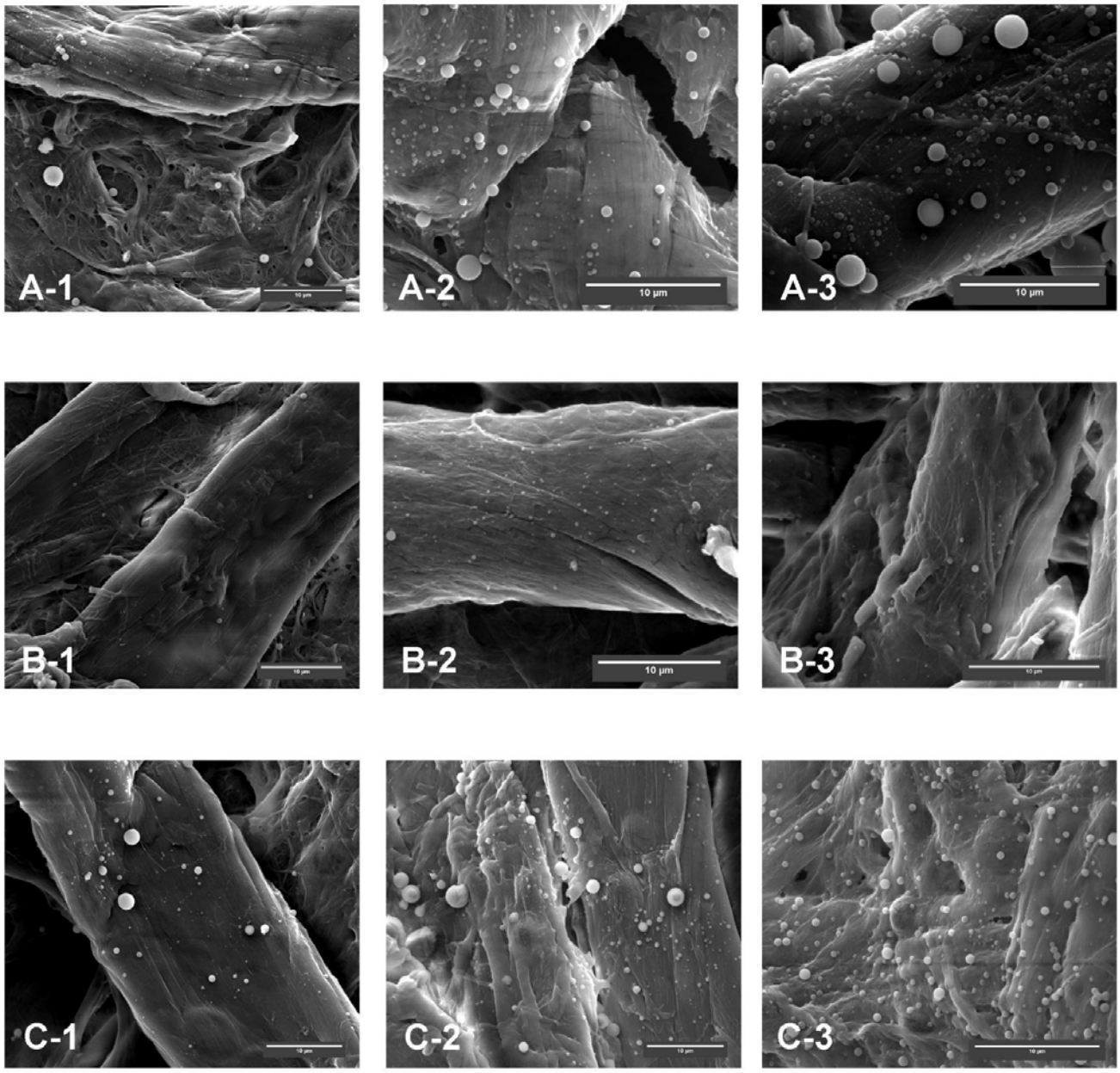

Figure 1. SEM of pure cellulose with lignin isolated from wheat straw (A-1, 2, 3), bagasse (B-1, 2, 3) and poplar (C-1, 2, 3) after dilute acid pretreatment at 120°C for 40 min (series A, B, C-1), 150°C for 20 min (series A, B, C-2) and 180°C for 10 min (series A, B, C-3); each is shown with 10 µm scale bar.

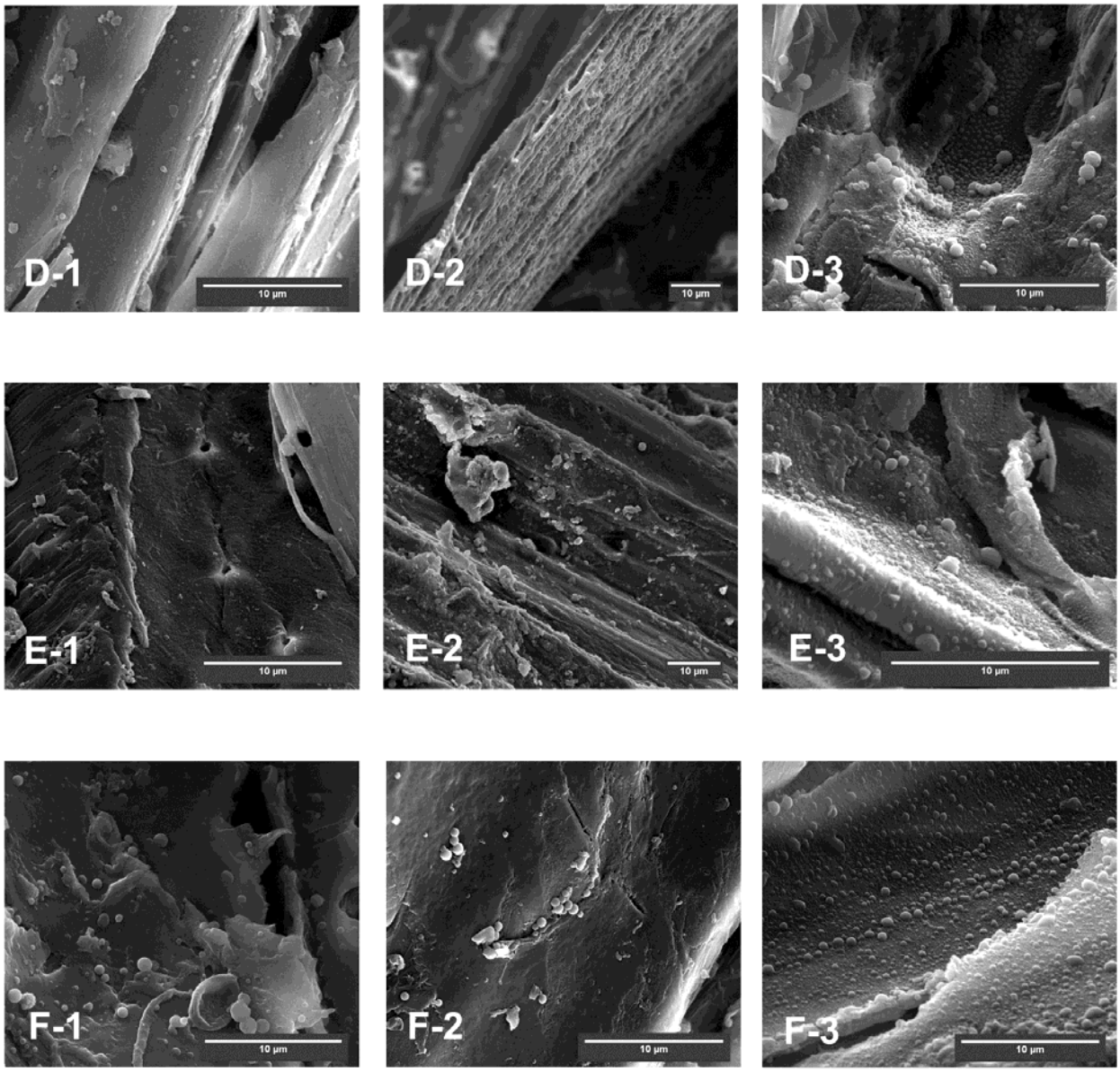

Figure. 2. SEM of whole biomass after pretreatment; wheat straw (D-1, 2, 3), bagasse (E-1, 2, 3) and poplar (F-1, 2, 3) after dilute acid pretreatment at 120ºC for 60 min (series D, E, F-1), 150ºC for 30 min (series D, E, F-2) and 180ºC for 10 min (series D, E, F-3); each is shown with 10 µm scale bar.

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REACTIVITY AND STRUCTURAL ELUCIDATION OF ALKALI HARDWOOD LIGNIN FROM AQUEOUS FRACTIONATION PROCESS

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Alkali lignin was fractionated through pH selective precipitation using CO_2 acidification at room and elevated temperatures. The structural attributes that engender this phase partitioning behavior could indicate suitable applications of lignin from different pH fractions. Lignin structure is revealed through many spectroscopic means as well as wet chemical and chromatography. Overall, an increasing trend in abundance of hydroxyl groups, as measured by H^1-NMR, was observed as fractionation pH decreased. Both 2D-NMR and thioacidolysis suggested relatively constant S:G ratio (ca 1.8) in lignin fractionated at room temperature. On contrary, lignin fractionated at elevated temperature showed an obvious decline in S:G ratio as pH decreased. Alkali lignin fractionated at higher pH was found to contain higher relative abundance of β–O–4 linkages, which decreased as pH lowered. Gel permeation chromatography and quantitative C^{13}-NMR also were employed to further elucidate the structure of different pH fractions.

The reactivity of each fraction was evaluated in response to catalytic oxidation and thioacidolysis, both of which showed similar trends wherein higher pH fractions tended to produce more monomers. Correlating these oxidation results to structural analysis did not only underline the importance of β–O–4 linkages, but also implied an adverse effect of hydroxyl groups on lignin oxidative reactivity. These reactions serve as an example of how unique physical and chemical properties in each different pH fraction of lignin can be recovered for suitable applications.

REFORMING OF LIGNIN DERIVED TARS OVER CHAR BASED CATALYST USING Py-GC/MS

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Tar removal is one of the major challenges in implementation of biomass gasification technology. Syngas tars cause formation of aerosols and soots, which plug filters, reactors and fuel lines. A char derived catalyst was tested in removal of tar produced from pyrolysis/gasification of kraft lignin in a pyroprobe reactor. Effects of reaction temperature (700, 800 or 900°C), water amount (5 to 10 µl), pressure (0.1 to 2.2 MPa) and atmosphere (inert or hydrogen) on catalytic conditioning of tar components were assessed. Tar components were analyzed by GC/MS.

Catechols were the most abundant, followed with phenols and guaiacols during noncatalytic kraft lignin gasification. The char based catalyst decreased lignin tar contents. An increase in reaction temperature led to an increase in removal efficiency of most tar components except naphthalene. Excessive water loading (10 µl) decreased the tar removal efficiency of char based catalyst. High pressure promoted the catalytic conditioning of lignin tar. Tar contents decreased when hydrogen was used as a gasification medium and thus promoted the conversion of lignin into noncondensable gas.

INSIGHTS INTO CELLULASE ENZYME INHIBITION BY THE HOT WATER HYDROLYZATES OF RICE STRAW

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Lignocellulosic biomass is an inexpensive and renewable source for industrial chemicals and biofuels production. However, lignocellulosic material, such as rice straw, is inherently recalcitrant to biochemical conversion, which usually involves enzymatic hydrolysis and fermentation. To overcome recalcitrance, chemical, physicochemical, mechanical and biological pretreatments are performed to condition the biomass prior to biochemical conversions (Kumar et al., 2009). Regrettably, these pretreatments also lead to the formation of byproducts that inhibit cellulolytic enzymes and fermentative microorganisms. Since cellulolytic enzymes contribute up to 14% of cellulosic ethanol production costs (Holcomb and Kenkel, 2014), understanding cellulase inhibition can pave the way for developing mitigation strategies and enhancing enzymatic saccharification efficiency.

Previously, we demonstrated that a 52 min 220 °C water pretreatment of rice straw released water soluble compounds, such as furans (2%), weak organic acids (37%), phenolics (6%) and xylooligosaccharides (24%) into the prehydrolyzate (Rajan and Carrier, 2014). The addition of 10 g/L of 220°C water hydrolyzate reduced exocellulase enzyme activity up to 80%. To determine which compounds were responsible for exocellulase inhibition, the 220°C water extract from rice straw was separated by centrifugal partition chromatography (CPC). Incubation with 8 g/L of CPC purified fractions of phenolics, furans, acetic and formic acids, and xylooligosaccharides, inhibited the exocellulase enzyme conversion rates by 75, 60, 60 and 45%, respectively. Although the initial hydrolysis rates of exocellulase were inhibited in the presence of the oligosaccharides xylotetraose and xylopentaose, its overall substrate conversion efficiency improved with time. To improve efficiency of the exocellulases, it was important to mitigate the phenolic compounds, because these compounds, even at concentrations of 1 g/L, were inhibitory to the enzymatic saccharification system. In future protocols, lignocellulosic pretreatment may be done such that the presence of soluble lignin derived byproducts is minimized.

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ENHANCED VOLATILE FATTY ACIDS PRODUCTION WITH OXYGENATION DURING ANAEROBIC DIGESTION OF LIGNOCELLULOSIC BIOMASS

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Volatile fatty acids (VFAs) are organic acids with carbons C_2 to C_5 produced during the acidogenic stage of anaerobic digestion (AD). These VFAs are precursors for many high value biobased chemicals and bioenergy (Surendra et al, 2015). Microoxygenation is an alternative approach that facilitates the biodegradation of lignocellulosic biomass. A proper amount of oxygen added could enhance hydrolysis and the acidogenesis process by promoting facultative microorganisms (Lim and Wang, 2013). A series of batch experiments were conducted to investigate the effect of microoxygenation on VFAs production from lignocellulosic biomass under mesophilic conditions. Napier grass was used as the substrate and oxygen was injected into the mixture of biomass and inoculum at dosages (mlO_2/gVS_{added}) of 0 (R1), 7 (R2), 14 (R3), 21 (R4) and 27 (R5) just before the start of the experiment. There was enhanced VFAs production with increasing O_2 dosage. R4 showed the highest VFAs production but it was not different than from R3. With respect to control (R1), R3 and R4 produced more than double the amount of VFAs. This could be associated with an increase in the population of facultative microorganisms (Botheju and Bakke, 2014) and the enhanced hydrolytic extracellular enzymes production (Johansen and Bakke, 2006) during microoxygenation. Moreover, VFAs production had a strong quadratic correlation with O_2 dosage with R2 of 0.96. With regards to the regression equation, it is predicted the optimal O_2 dosage to produce the highest amount of VFA is 19.3 ml O_2/gVS_{added}. Methane production showed a decreasing trend with increasing O_2 dosing. This phenomenon could be from the increase of VFAs concentration in the liquid phase, which would have inhibited methanogens (Botheju and Bakke, 2014). Therefore, microoxygenation is an alternative method that can be applied to increase the production of VFAs from AD of lignocellulosic biomass.

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PRODUCTION OF BIOSURFACTANTS USING *BACILLUS SUBTILIS* ON PRETREATED BIOMASS HYDROLYSATES IN 5-L FERMENTOR

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Surfactin is a *Bacillus subtilis* biosurfactant which has excellent surface active properties but has limited aqueous solubility. Recombinant strain of surfactin producing *B. subtilis* (E4088) produces a water soluble variant of surfactin called FA-glu due to a less hydrophobic amino acid structure than surfactin (Reznik et al., 2010). In a study using 50 mL shake flask fermentations for both strains, soy hulls, alfalfa and switchgrass were chosen as the best carbon sources compared to glucose for highest growth and product concentration for FA-glu and surfactin producing *Bacillus subtilis* strains. These three biomasses were pretreated with a combination of liquid ammonia and ultrasonication among six fibrous biomasses to generate hydrolyzates, utilized as carbon source in growth media for both *Bacillus* strains in 50 mL shake flask experiments. Glucose content and relative availability of hexose and pentose sugars in the hydrolysates played an important role in determining highest growth and product titer. 5-L fermentations were conducted where growth media based on these selected biomass hydrolysates as carbon source were studied for bacterial growth, economic efficiency and product concentration of surfactin and FA-Glu. Highest bacterial growth was observed for switchgrass based media fermentation for surfactin and FA-Glu producing strains. Highest concentrations of both products were observed to be in media containing soy hull hydrolysates (2.9 and 0.28 g/L for surfactin and FA-Glu, respectively). A technoeconomic analysis of the 5-L fermentation process showed that surfactin cost estimate in our process was $45.70/g, compared to the market price of $13.94/mg ($13,940/g).

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EFFECT OF LIMITED AIR EXPOSURE AND COMPARATIVE PERFORMANCE BETWEEN THERMOPHILIC AND MESOPHILIC SOLID STATE ANAEROBIC DIGESTION OF SWITCHGRASS

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Solid state anaerobic digestion (SS-AD) is a promising method for the conversion of switchgrass into biogas (~60% methane, ~40% carbon dioxide) for energy production. SS-AD has several advantages compared to traditional liquid AD (L-AD), such as reduced water and heating requirements. A common practice in L-AD systems is to supply small amounts of air to the digester headspace because limited air exposure can enhance substrate degradation and reduce hydrogen sulfide (H_2S) content in biogas. However, this practice has been tested sparingly during SS-AD. The effects of air exposure and total solids (TS) content on SS-AD performance were evaluated under mesophilic (37°C) and thermophilic (55°C) conditions. Limited air exposure did not influence the methane yield during SS-AD of switchgrass, indicating air exposure could be used to reduce H_2S in commercial SS-AD systems. Thermophilic SS-AD increased methane yields and organic component degradation compared to mesophilic SS-AD. Operation of SS-AD at high TS content (30%) resulted in reduced methane yields. Thermophilic and mesophilic SS-AD of switchgrass produced positive net energy based on a theoretical "garage type" SS-AD system operating in a temperate climate.

ANAEROBIC DIGESTION OF LIGNOCELLULOSIC BIOMASS USING RUMEN CONTENTS AS INOCULUM FOR ENHANCED BIOGAS PRODUCTION

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Lignocellulosic biomass can act as an attractive and sustainable feedstock for biogas production via anaerobic digestion (AD) due to low price, large scale availability and relatively high biomass yield (Xia et al., 2012). However, the refractory property of lignocellulosic biomass makes hydrolysis, the first step of AD, the rate limiting step which leads to less biogas yield (Noike et al., 1985). Since the microbial community in the rumen facilitates the degradation of lignocellulose in animal food, the use of rumen contents as an inoculum could be a strategy to enhance biogas production from lignocellulosic biomass.

Three anaerobic bioreactors (R1, R2 and R3) were operated to evaluate this strategy for the codigestion of Napier grass (*Pennisetum purpureum*) and cow manure. R1 was inoculated with rumen contents, R3 with a conventional anaerobic digestion inoculum and R2 with a mixture of both inocula. Changes in the microbial community structure during start up phase also were assessed. R2 exhibited the highest archaea/bacteria diversity including hydrolytic rumen bacteria, syntrophic bacteria and methanogens. The combination of rumen contents and conventional anaerobic digestion inoculum can enhance the biodegradation of lignocellulosic biomass; however, further investigation will be conducted. Also, the start up period should be monitored and the use of a cosubstrate with high buffering capacity is recommended for the efficient digestion of Napier grass.

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COMPARING FLUID CRACKING CATALYST (FCC) AND SWITCHGRASS BIOCHAR DERIVED CATALYSTS FOR THERMAL DECOMPOSITION OF ACETIC ACID

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Biochar has yet to be tested for its catalytic properties. However, there are scattered suggestions that biochar with a few modifications may act as a catalyst for a variety of reactions. Biochar is attractive for its low cost and can be produced from renewable carbon sources, thus representing a value added coproduct from a thermochemical biorefinery. Four different catalysts, fluid cracking catalyst (FCC), switchgrass biochar (BC), biochar impregnated with nickel nitrate (BCNi) and biochar deposited with iron oxide (BCFe) were tested and compared for conversion of acetic acid, a chosen biooil model compound, in a custom made, continuous flow reactor operated at 450°C.

Biochar derived catalysts had catalytic activity comparable to the FCC catalyst. Conversion rates were 5.55, 17.33, 15.21, and 12.41% for the blank (no catalyst), BC, BCNi and FCC catalysts, respectively; while BCFe had the highest conversion of 40.66%. (Singh and Poggi, 2015).

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HYDROTHERMAL CARBONIZATION OF SPENT OSMOTIC SOLUTION GENERATED FROM OSMOTIC DEHYDRATION OF BLUEBERRIES

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Hydrothermal carbonization of spent osmotic solution (SOS), a waste generated from osmotic dehydration of fruits, has potential to be transformed into hydrochars, a value added product, while reducing cost and overall greenhouse gas emissions associated with waste disposal. Osmotic solution (OS) and spent osmotic solution (SOS) generated from osmotic dehydration of blueberries were compared for their thermochemical decomposition behavior and hydrothermal carbonization. OS and SOS samples were characterized for total solids, elemental composition and thermogravimetric analysis (TGA). In addition, hydrothermal carbonization was performed at 250°C and 30 min to produce hydrochars. The hydrochars were characterized for elemental composition, Brunauer-Emmett-Teller (BET) surface area, particle shape and surface morphology.

SOS sample lost more weight in the lower temperature range than the OS sample. Both samples produced, approximately, 40 to 42% (wet feed basis) hydrochar during hydrothermal carbonization but with different properties. The OS sample produced hydrochar, which had spherical particles of 1.79 ± 1.30 μm diameter with a smooth surface. In contrast, the SOS sample produced hydrochar with no definite particle shape but with a raspberry like surface (Singh and Sivanandan, 2014).

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COPROCESSING OF PYROLYSIS VAPORS WITH BIOCHARS FOR EX-SITU UPGRADING

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Coprocessing of woody biomass with two biochars (made from switchgrass or red oak bark) was studied as a way of upgrading the pyrolysis vapors. Clean woodchips were pyrolyzed with and without biochars under atmospheric pressure at the target temperature of 500°C. The coprocessing with both biochars had influences on biooil yields, moisture content and pH value of biooils.

However, the vapor upgrading process decreased the carbon yield of biooil when using switchgrass biochar for coprocessing. The biooil yield decreased from 49.31 (nonbiochar) to 44.81% with switchgrass biochar and to 48.68% with biochar from red oak bark. The lost mass of biooil ended up in the gaseous phase as reflected in increased contents of carbon dioxide and carbon monoxide. The gaseous phase composition of hydrogen increased from 0.82 to 3.74%, of carbon dioxide from 21.16% to 32.33 % and of carbon monoxide from 16.49 to 23.19% with the addition of switchgrass biochar compared to nonbiochar pyrolysis (Jin et al., 2015).

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INCREASING ALGAE MEAL DIGESTIBILITY FOR USE IN FISH DIETS

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Rapid increase in the consumption of aquaculture products has led to an increased demand for fish meal as a primary protein source in carnivorous fish diets. Harvest levels of wild catch fish species already exceed the sustainable level (Patterson and Gatlin, 2013). Rising demand and limited supply of fish meal have led to increased prices and use of alternative protein sources. An alternative is algae meal (Patterson and Gatlin, 2013; Vizcaíno et al., 2014). However, low digestibility of algae meal limits the amount that can be incorporated into fish diets.

The low digestibility of algae meal is attributed to the rigid cell wall of microalgae; therefore, a cell lysis method was proposed to disrupt the algal cell wall and increase the algae meal digestibility. Several methods, including enzymatic lysis, high pressure and ultrasonication, proposed in studies (Gerken et al., 2012; Halim et al., 2013) for algal cell disruption are costly or energy intensive. We propose a novel continues system which is energy and cost efficient. Our strategy consists of rapid heating of algae slurry under pressure followed by a rapid depressurization in a flash tank. The process is aided by enzymes to further degrade the algae cell walls. Optimum temperature and pressure for maximum degradation of cell wall was devised based on first principles from the models of algae cell wall. The model was validated experimentally in a custom built continuous algae treatment system. A slurry pump was used to pump the 10% algae slurry through a 1.27 cm stainless steel tube. The algae slurry was heated to 150°C at 4.0 bar pressure and rapidly depressurized in a flash tank. Due to its accuracy and reproducibility, cell lysis was quantified by cell counting. The number of intact cells remaining after flashing out the slurry were counted by microscopic observation using a haemocytometer with a 100 μm chamber depth (Yap et al., 2015). We expect 70% of cells will be lysed after algae treatment.

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PHYTIC ACID CONCENTRATOIN AND PHYTASE ADDITION EFFECTS ON FOULING CHARACTERISCTICS OF STEEPWATER

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Heat transfer fouling is descriptive of the phenomenon of unwanted materials forming and accumulating on heat transfer surfaces. This can lead to a decrease in process efficiency, as fouling of heat transfer equipment increases energy consumption and maintenance costs. In the corn wet milling industry, evaporator fouling takes place as steepwater is concentrated. Steepwater results from the corn steeping process and is composed of solubilized kernel compounds, microbes (principally *Lactobacilli*) and solids from recycled process streams.

Research on corn processing fouling has been focused on effects of steepwater solid, corn oil, pH, Reynolds number, solids concentration and carbohydrates (Agbisit et al., 2003, Singh et al., 1999, Wilkins et al., 2006ab, Arora et al., 2010, Challa et al., 2014). However, effects of phytic acid concentration or phytase addition on the fouling characteristics is not known. There are reports from industry suggesting phytic acid content is correlated positively with fouling rate and adding phytase to the process stream may reduce fouling. Researchers also have shown the solubility of certain phytic acid metal complexes, the product of chelation reaction between metal ions available in corn process streams (Mg, Ca, K) and phytic acid, can be influenced by adding phytase (Ekholm et al., 2003). Investigators studying one of these phytic acid metal complexes (Ca) concluded concentration was correlated positively with fouling in the dairy industry at high temperatures (Bansal et al., 2006). Our purpose was to evaluate effects of phytic acid concentration and phytase addition on steepwater fouling behavior. Experiments were conducted using commercial steepwater with different phytic acid concentrations. Phytic acid concentrations of the samples were adjusted to vary from 25 to 75 mg/g sample. Fouling resistances were measured using an annular probe with a 7 L batch system. Mean fouling rate, maximum fouling resistance and induction period characterized fouling behavior. We will provide an understanding of phytic acid effects on fouling and provide potential solutions to mitigate fouling in the wet milling process.

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ENHANCED ENZYMATIC DIGESTIBILITY OF *MISCANTHUS X GIGANTEUS* BY SOLID STATE FUNGAL PRETREATMENT WITHOUT STERILIZATION

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Miscanthus is an energy crop with potential for the biofuels industry, because of its high annual biomass yields, low nutrients and water requirements, and adaptability to different climate and soil conditions (Heaton et al., 2008). Since the lignocellulosic structure of miscanthus is recalcitrant to digestion, pretreatment is needed to enhance sugar release during the sequential enzymatic hydrolysis (Brosse et al., 2012). Thermochemical pretreatment methods operate under harsh conditions and have a large water footprint. In contrast, fungal pretreatment can be performed under mild conditions, using minimal amounts of chemicals and water. However, a costly feedstock sterilization step is required prior to fungal pretreatment, to eliminate negative impacts of indigenous microorganisms (Wan and Li, 2012). Using precolonized feedstock as the inoculum is a promising strategy to address this issue but has not been studied in fungal pretreatment of grassy biomass, such as *Miscanthus* (Zhao et al., 2014).

We conducted fungal pretreatment of nonsterile *Miscanthus* × *giganteous* with *Ceriporiopsis subvermispora* using previously colonized *Miscanthus* as an inoculum. Five different inoculum ratios (10, 20, 30, 40 and 50%) and two moisture contents (60 and 75%) were tested. Inoculum ratios equal or greater than 30% enhanced the enzymatic digestibility of *Miscanthus* 3 to 4 fold, which was consistent with the lignin degradation during pretreatment. Sugar loss, up to 24% during fungal pretreatment, was observed but the final sugar yield could be improved 2.5 to 4 fold.

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VALUE ADDED CONVERSION OF LIGNIN RICH RESIDUES FROM CELLULOSIC ETHANOL PRODUCTION

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Value added conversion of lignin rich residues from bioethanol plants has received attention recently due to increasing production of cellulosic ethanol. Methanol fractionation was employed to extract and isolate lignin for further processing. The obtained lignin fractions were depolymerized into aromatic monomers via hydrogenolysis at mild temperature. Methanol soluble lignin fraction was converted into monomers as compared to raw biorefinery lignin and methanol insoluble fraction. Oxidation of lignin fractions via hydrogen peroxide altered functional groups in lignin subunits and resulted in the formation of aldehydes and carbonyl groups but did not enhance the yields of aromatic monomers.

LIGNIN TO BIOFUELS AND BIOMATERIALS

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Leveraging funded projects from DARPA, NSF, DOE-NREL, Sun grant-DOT and JCATI, we demonstrated novel principles of catalytic upgrading of biomass derived lignin to biofuels and chemicals. Combinations of noble metal catalysts (eg, Ru/Al_2O_3, Ru/C, Ru/graphene) in the presence of various acids (eg, $ZnCl_2$, $AlCl_3$ and zeolites, including H^+-ZSM-5, H^+-Mordenite, H^+-Y and Beta- ZSM-5) were tested for hydrodeoxygenation (HDO) activity of technical lignins from different sources (eg, corn stover, poplar wood and lodgepole pine). Generation of hydrocarbon (C_7-C_{18}) derivatives from biomass derived lignin with high selectivity of C_{12} to C_{18} cyclic structure hydrocarbons via the cleavage of C–O–C bonds without disrupting the C–C linkages (8–8', 8–5' and 5'–5''/β–O–4') in the lignin structure.

Reactivity and structural features of technical lignins are key factors of catalyst selection in presence of hydrogen for producing a wide variety of hydrocarbon species (aliphatic and aromatic) that are found in jet fuel blend stocks. In addition, the reactivity of lignin and its interactions with the chemical catalysis systems were studied to reveal the principles of the reaction mechanism, its control and applications (Lasker et al., 2013a, 2013b, 2014). Also, we are funded through DOE to better understand the biological processing of biomass derived lignin to lipids for biofuel production. This project is in collaboration with TAMU, Georgia Tech and UBC on a joint research effort to engineer multiple microbial species (eg, *Rhodococcus opacus* and *Pseudomonas putida)* and investigate the biological pathways for converting lignin to fuels and other valuable products. Wild type and genetic engineered strains were able to convert lignin and accumulate lipids for fuel production (Xie et al., 2015).

Another research effort is focused on synthesis of biopolymers from lignin (eg, supercapacitor). We seek to define avenues to convert lignin to lower cost biopolymers through applications of our learning. This is a joint effort with PNNL, NREL and TAMU. We demonstrated a simple and efficient one step method to obtain high surface area porous carbons from renewable and low cost lignin precursors. These carbonized lignins had relatively high electrochemical performance in terms of specific capacitance, energy density and power with good capacity retention (Jeon et al., 2015).

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COMPARISON OF FERMENTATION CHARACTERSITICS BETWEEN PIGMENTED CORN AND YELLOW DENT CORN IN TWO DRY GRIND PROCESS METHODS

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In a dry grind ethanol plant, distillers dried grains with solubles (DDGS) is the main coproduct which is used mainly in ruminant animal diets. Increasing the value of DDGS will improve the profitability of the dry grind ethanol process. Pigmented corn, which is rich in anthocyanin content, is an alternative feedstock for dry grind process but the effects of anthocyanin on fermentation characteristics in dry grind process are not known. The effect of anthocyanin in conventional (conventional starch hydrolyzing enzymes) and modified (granular starch hydrolyzing enzymes, GSHE) dry grind processes was evaluated. Ethanol conversion efficiencies of pigmented corns (78.4±0.5% for blue corn, 74.3±0.4% for red corn and 81.2±1.0% for purple corn) were comparable to that of yellow dent corn (75.1±0.2%) in both the conventional dry grind process and the modified dry grind process, using granular starch hydrolyzing enzyme (GSHE) (83.8±0.8% for blue corn, 81.1±0.3% for red corn, 93.5±0.8% for purple corn and 85.6±0.1% for yellow dent corn). The modified process uses GSHE to replace the high temperature liquefaction, which improves the anthocyanin stability in the process (Patras et al., 2011). Pigmented corn with rich anthocyanin content did not have a negative effect the fermentation characteristics for dry grind process; therefore, there is a potential to use pigmented corn in dry grind process, especially using GSHE.

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HARVEST LOGISTICS TRACKING FOR BULK FORMAT SWITCHGRASS

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Movement and interactions of seven pieces of harvest and transport equipment were logged with global positioning system (GPS) tracking during the harvest of field chopped switchgrass hauled to a storage depot. The GPS tracking provided the basis for calculated equipment functions and interactions, without use of CAN-bus systems or operational sensors or researcher distractions in operator cabs. Researchers recorded nonintrusive field notes, such as tip wagon unload points, to facilitate geographic information systems (GIS) analysis of custom, logical expressions to categorize all 1 second track log data entries for each piece of equipment. Categorization enabled the computation of turn times, field efficiency, utilization, equipment capacity and system capacity, and ultimately system limiting factor apportioned to each piece of equipment. Load weights were determined with commercial truck scales.

We harvested 100 ha of switchgrass (SG), yielding 690 DMg of chopped SG delivered to a storage depot within a mean haul distance of 9.1 km. The harvest campaign was active 14 days during the winter, averaging SG moisture content of 13.45% (wb), mean effective field capacity of 7.15 ha day^{-1} and a mean SG yield of 6.9 DMg ha^{-1}. Fields of varying geometries were harvested with mower conditioner turn times ranging from 1.83 to 7.97 min ha^{-1} and pull type forage harvester turn times ranging from 2.47 to 12.10 min ha^{-1}; lowest turn times were in fields with long straight rows. Efficient biomass harvest logistics need improved field geometry that reduces turn times due to point rows or scattered production areas that reduce or inhibit continuous processing at full rated equipment width, and reduced haul distances. The pull type forage harvester had 84% productive time proportion and 16% unproductive time proportion mostly spent (13%) waiting on an empty tip wagon. Mean throughput (and mean field efficiency) observed for mower conditioner and forage harvester were 16.0 DMg h^{-1} (68.3%) and 7.6 DMg h^{-1} (72.6%), respectively. For transport equipment, daily mean utilization was 62.5% for tip wagons and 69.1% for trucks. The forage harvester was the overall system's most common limiting factor, as planned, limiting the system an average of 88.7% of total daily operating time. On road trucks were the next most frequent limiting factor, ranging from 1.3 to 23.4%, averaging 9.6%. The highest limitation value for on road trucks was on the first day due to an unforeseen operational incident at the depot that limited unloading. System limitation due to tip wagons ranged from 0 to 4.3%, averaging 1.7%. Overall system capacity averaged 7.4 DMg h^{-1}. About two harvest days from start of the campaign were required to reach or exceed the mean capacity, which was suggestive of a combination of an operator learning curve, advancing team dynamics and equipment system commissioning.

FAST MICROWAVE ASSISTED CATALYTIC GASIFICATION OF BIOMASS FOR SYNGAS PRODUCTION AND TAR REMOVAL

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Biomass is a carbon neutral energy source (Mckendry, 2002); efficient uses of biomass are considered promising in the future energy portfolio (Richardson et al., 2012). Among all the utilization technologies, the production of syngas from biomass gasification is considered as an attractive route to produce chemicals, biofuels, hydrogen and electricity (Damartzis and Zabaniotou, 2011). It has been estimated that syngas production from biomass accounts for at least half, and in many cases more than 75%, the cost of biofuel production. Therefore, successful development of cost effective processes for high quality syngas production will promote biomass utilization.

A microwave assisted biomass gasification system was developed for syngas production. Three catalysts, including Fe, Co and Ni with Al_2O_3 support, were examined and compared for their effects on syngas production and tar removal. Microwave irradiation is an effective heating method for biomass gasification. Ni/Al_2O_3 was found to be the most effective catalyst for syngas production and tar removal. The gas yield reached 80% and the composition of tar was the simplest when Ni/Al_2O_3 catalyst was used. The optimal ratio of catalyst to biomass was determined to be 1:5 to 1:3. The addition of steam was found to improve gas production and syngas quality. Using XRD analyses, it was demonstrated that Ni/Al_2O_3 catalyst has good stability during gasification process.

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FLOWTHROUGH PRETREATMENT OF BIOMASS FOR FERMENTABLE SUGARS AND REACTIVE LIGNIN PRODUCTION

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An important challenge of cellulosic biorefining has been, and continues to be, the development of effective and low cost pretreatment technology. The water based pretreatment of biomass is developed as a platform for production of sugars and lignin showing advantages in cost, mass transfer, hydrolysis kinetics and fluid properties. To date, many potentially economical and scalable pretreatment options for biorefineries are aqueous based (Wooley et al., 1999, Yang and Wyman, 2008, Pretreatment, 2011, Davis et al., 2013). Various biomass feedstocks (poplar wood, corn stover, and pine wood) with different particle sizes prepared through different cutting approaches were pretreated in a flowthrough system under different conditions (ie, temperature 220 to 300°C for 0 to 40 min, pH 2 to 12 and flow rates of 0 to100mL/min) to assess effects on yields of hemicellulosic sugars, cellulosic sugar, lignin and enzymatic hydrolysis of the whole slurries.

Application of flowthrough pretreatment enhanced sugar and lignin recovery and limited carbohydrates degradation loss. However, carbohydrates underwent severe peeling off degradation to carboxylic acids under pretreatment severities and high pH conditions. More importantly, hardwood and softwood lignin presented different kinetics in delignification and recondensation, resulting in differed pretreated solid biomass residues. A kinetic model involving solubility and mass transfer effects was developed to simulate flowthrough pretreatment data. The effects of particle sizes and cutting approaches were related to pretreatment mass transfer efficiency. These new findings provide deeper insights into the kinetic changes during aqueous flowthrough pretreatment.

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TEMPERATURE EFFECTS ON HEAT TRANSFER FOULING OF THIN STILLAGE FROM ETHANOL PRODUCTION

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Heat transfer fouling is the formation and accumulation of unwanted materials on heat transfer surfaces, which leads to a decrease in the overall heat transfer coefficient. Fouling of heat transfer equipment increases energy consumption and maintenance costs and thus decreases processing efficiency. In the fuel ethanol industry, evaporator fouling occurs when thin stillage is concentrated. Fouling affects the efficiency and environmental footprint of more than 200 biorefineries in the US. Thin stillage is the liquid fraction of unfermented materials from fermentation and is composed of carbohydrate, protein, fat and ash.

Research on thin stillage fouling has been focused on effects of corn oil, pH, Reynolds number, solids concentration and carbohydrates (Singh et al., 1999, Wilkins et al., 2006ab, Arora et al., 2010, Challa et al., 2015). However, temperature effects on fouling rates have not been studied. Our objectives were to investigate the influence of bulk fluid temperature, initial probe temperature and their temperature difference on thin stillage fouling characteristics. Experiments were conducted using model thin stillage (1% starch solution) and commercial thin stillage with varying temperature conditions. Bulk temperatures were varied from 60 to 80°C and initial probe temperatures were varied from 100 to 120°C; thus, temperature differences varied from 20 to 60°C. Fouling resistances were measured using an annular probe with a 7 L batch system. Mean fouling rate, maximum fouling resistance and induction period were used to characterize fouling behavior.

For commercial thin stillage, fouling rate and maximum fouling resistance increased as the initial probe temperature increased from 100 to 120°C. At 120°C initial probe temperature, fouling rate increased with bulk temperature. Using model thin stillage, similar results were observed. An induction period of 5 hr was observed for model thin stillage at initial probe temperature of 100°C. Induction period of model thin stillage increased and maximum fouling resistance decreased with decrease of bulk temperature. Using higher initial probe temperature, such as 120°C, and fluid bulk temperature of 80°C would provide repeatable and more rapid (within 5 hr) characterization of fouling behavior.

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D-LACTIC ACID PRODUCTION FROM CORN STOVER USING GENETICALLY ENGINEERED *LACTOBACILLUS PLANTARUM*

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The thermostability of polylactic acid (PLA) is maximized when poly-L-lactic acid (PLLA) and poly-D-lactic acid (PDLA) are blended at 1:1 ratio; as a consequence, the demand for optically pure D-lactic acid is increasing (Abdel-Rahman et al., 2013). To make the biotechnological production of D-lactic acid feasible and effective, low cost lignocellulosic biomass utilization is essential. However, xylose derived from hemicellulose portion of lignocellulosic biomass is not used by most lactic acid bacteria, which results in inefficient sugar utilization and low lactic acid yield. Our objective was to construct a recombinant lactic acid system that can simultaneously use all major sugars derived from corn stover to produce D-lactic acid at high optical purity.

A xylose assimilation plasmid pLEM415-*xylAB* was constructed by cloning xylose assimilation genes from *L. brevis* and introduced into an L-lactate deficient strain, *L. plantarum* NCIMB 8826; the resulting recombinant strain was designated as *L. plantarum* Δ*ldhL1*-pLEM415-*xylAB*. Corn stover and soybean meal extract (SBME) were evaluated as cost effective raw materials for D-lactic acid production by this recombinant strain. Simultaneous use of glucose and xylose derived from corn stover was achieved and high optical purity D-lactic acid was produced (optical purity >99%). D-lactic acid yield was 0.77 g g^{-1} when corn stover and SBME were used to replace synthetic sugars and expensive yeast extract in a fed batch fermentation. This fermentation process has the potential to reduce the production cost of D-lactic acid since the recombinant strain effectively utilized all biomass derived sugars and SBME as nitrogen sources.

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ORAL PRESENTATIONS

WHY I AM OPTIMISTIC ABOUT THE US BIOECONOMY

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The current state of the US bioeconomy will be reviewed, including the emerging cellulosic industry and established biorefineries for pulp and paper, sugar, and corn processing. Prognostications will be made for future industry trends. Technical, business and policy hurdles for the industry will be identified and ways these hurdles are being addressed in new projects. The relative contributions of biofuels, biochemicals and biomaterials also will be covered.

AN OVERVIEW OF BIOFUELS AND BIOPRODUCTS

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Biofuels and bioproducts have been the subject of significant investment in research and capital over the last 20 years. Many companies have been established to produce these materials in competition with their petroleum counterparts. Recent headwinds have arisen with regard to fossil fuel price reductions and government policy causing some companies to pull back, change focus or recede from the market. The first wave of change occurred about 3 years ago with many companies, such as Solazyme and Amyris, that were founded to produce fuels changing focus to the more achievable and higher margin chemicals market. Mergers and acquisitions have been the prevailing theme over the last several months with many companies such as Mascoma, Virdia, Verenium, LS9 and Cereplast being acquired by others. More disturbing are bankruptcies or asset liquidations by several companies such as OPX Biotechnologies, KIOR, Cobalt Technologies, TMO Renewables and Range Fuels. While troubling, these moves can be seen as natural maturation of a marketplace where those companies with the best technology, business plan and people will shake out in the months and years to come.

While these market forces are significant the fundamental drivers for achieving a sustainable chemical and fuels industry remain unchanged:

1) reliance upon a finite resource for production of materials so critical to our way of life seems both short sighted and morally questionable,
2) the vast majority of scientists concur that climate change is real and due to human activity, primarily the burning of fossil fuels,
3) public sentiment continues to indicate that sustainable products are preferred even if only a small number of people are willing to pay more and
4) understanding of metabolic pathways and the development of tools to manipulate the genetic code of organisms has been described as the greatest technological advance of this century with implications broader than those of the industrial revolution of the 19th century or the computer revolution of the 20th.

These drivers will not change and the industry will march forward, perhaps not at the pace anticipated by early enthusiasts but steadily and with great rewards for those who prevail.

TOWARDS A SUSTAINABLE TIRE AND RUBBER INDUSTRY

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As sustainable growth on the mobility of our society requires effective utilization of limited resources, we as users' industry would continue enforcing reduce, reuse and recycle efforts along with cooperation for stable ensuring of natural and synthetic rubber, textile, additives, reinforcement filler etc. Furthermore, for making the use of rubber resources as a sustainable material, we need to work in support of improving productivity of natural rubber and developments of new materials for ensuring a stable supply of rubber materials globally because a tire as an essential component for both cars and trucks is an important factor as we have to consider the environmental effects of mobility in the future. This means our activities as a tire manufacturer may have a significant impact on resource conservation and protection of the global environment.

Therefore, with our "Environmental Mission Statement" as our guide, we are working comprehensively toward the realization of a sustainable society. In particular, we are committed to the "realization of 100% sustainable materials" which is our unique concept, and where we will be able to implement our strength.

Three basic objectives for the realization of a sustainable society will be presented with examples. In these initiatives, making efforts to balance between conservation of the biodiversity and increasing supply capacity of the rubber also will be discussed. Considering the need to conserve and protect tropical rainforests and the disease risks of Hevea rubber trees, we need to develop alternative rubber that can be harvested in a wider geographic region. Guayule and TKS are two possible candidates for rubber production. Focusing on the potential of Guayule and TKS as the possible alternative to Hevea rubber, Bridgestone has started research and development activities on these plants.

CURRENT STATUS OF BIOBASED FUELS AND CHEMICALS

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Beginning with the first energy crisis in the early Seventies, the energy independence movement led to use of renewable resources to supplement fossil resources. This began with the production of ethanol for fuel using agricultural commodities such as grain or sugar. More recently, the move towards not only greater volumes of renewable fuels, but also biobased chemicals, has been driven by concerns about anthropogenic climate change. Together, these issues have led to greater emphasis on replacing traditional fossil resources to not only produce fuels but also chemicals from "bio" materials and establish a sustainable "green" industry based upon renewable resources.

We will discuss what constitutes biofuels and biochemicals, available feedstocks and platforms used in their production and review a list of products currently in development. We also will discuss key players in these emerging markets.

AUTHOR AND AFFILIATION INDEX