ANNUAL REPORT
COMPREHENSIVE RESEARCH ON RICE
April 1, 2010 – December 31, 2010

PROJECT TITLE: Strategies leading to novel nano-materials and performance industrial products

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LEVEL OF 2010 FUNDING: $53,500

OBJECTIVES AND EXPERIMENTS CONDUCTED TO ACCOMPLISH OBJECTIVES:

The objectives of this project are to: 1) separate rice straw components; 2) convert them to novel nanomaterials and advanced functional products. The goal for separation or fractionation is to derive the four major rice straw components: cellulose, hemicellulose, lignin and silicon via most streamlined pretreatment processes. The goal for conversion of these components to potentially novel and high performance industrial products include: a) cellulose nanocrystals (CNCs); b) advanced cellulose fibers for membranes and composites; c) porous carbon fibers and carbon nanofibers; and d) silicon carbide (SiC) nanowires.

The experiments conducted on proposed objectives are briefly summarized as follows.

Objective 1. Separation of rice straw components
Rice straw was washed with water, dried and milled to pass through 60-mesh screen. In all cases, the waxes were removed by extraction (2:1 v/v toluene/ethanol, 55^{o}C, 24 h). In developing streamlined fractionation processes to derive the major rice straw components, two pathways were targeted: a) to derive the purest form of cellulose at the highest yield, and b) to collect hemicellulose, lignin and silicon, either individually or together, to the highest yield.

1a. Cellulose fractionation by acidified sodium chlorite and potassium hydroxide process
The dewaxed powder was delignified with 1.4% acidified sodium chlorite at pH 3.0-4.0, adjusted with glacial acetic acid, under constant stirring at 70 °C for 5 h. The reaction was stopped by quenching with ice and the solids were precipitated, washed by copious amount of water until neutral and filtered. Hemicellulose was leached with 5% potassium hydroxide at ambient temperature for 24 h and then at 90 ^{o}C for 2 h. The solids were washed by copious amount of water until neutral and filtered. The aqueous sample suspension was quickly frozen by liquid nitrogen and then freeze-dried.

1b.1. Isolation of lignin and hemicellulose by sodium chlorite/potassium hydroxide process
Lignin is precipitated from the supernatant of acidic sodium chlorite reaction (1.4 wt% $NaClO_2$, pH 3–4) at 70°C for 6 h by adding 10 M NaOH to pH 10. Hemicellulose is then extracted with 5 wt % KOH (70°C for 24 h) from the solid residue.

1b.2. Isolation of hemicellulose and lignin by alkaline peroxide process

Hemicellulose and lignin may be precipitated by evaporation of ethanol from the filtrate of reaction with 1 wt % NaOH (55°C for 2 h) and 3 volume of ethanol added. The solid residue may be reacted with 2.0 % H_2O_2 (w/v) at a 50:1 liquid-to-solid ratio, adjusted to pH 11.5 with 10M NaOH to yield yellowish cellulose that may be bleached with 1.4% $NaClO_2$.

Objective 2. Conversion of rice straw components
The pure cellulose was hydrolyzed in 64-65 wt% sulfuric acid at 45 °C for up to 45 min and the reaction was stopped by diluting with ice water. The cellulose nanocrystal gel was washed once and collected by centrifugation at 5000 rpm for 25 min at 10 ºC and then was dialyzed against ultra-pure water until neutral. The solid aggregates were disrupted by sonication, filtered, quickly frozen by liquid nitrogen and freeze-dried.

The pure cellulose was further hydrolyzed in 64-65 wt% sulfuric acid with an acid-to-cellulose ratio of 8.75 mL/g at 45 °C for up to 45 min. The reaction was stopped by dilution with 10-fold ice water to yield cellulose nanocrystal gel which was washed, centrifuged (5000 rpm for 25 min at 10 ^{o}C), then dialyzed until neutral pH. The solids in the suspension were disrupted by sonication for 30 min, filtered and freeze-dried. The cellulose nanocrystals were characterized by light microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Silica was extracted from rice straw by a two step process. Rice straw was first converted to ash by heating (10 °C/m) step-wise to 250, 325 and 575 °C, then chemically extracted in 0.5 M NaOH at 100 C for 4 h, neutralized in 10% H SO, filtered to generate silica.

SUMMARY OF 2010 RESEARCH (Major accomplishments) BY OBJECTIVES:

Objective 1. Separation of rice straw components
Two major separation/fractionation routes have been evaluated in detail and streamlined to derived the major components in rice straw, namely, cellulose, hemicellulose, lignin and silicon.

1a. Cellulose fractionation by acidified sodium chlorite and potassium hydroxide process
A straightforward and optimized three-step process has been established to extract pure cellulose from rice straw at an overall yield exceeding 36% (*Figure 1*). The de-waxing (toluene/ethanol), de-lignification (acidified sodium chlorite) and de-hemicellulose (potassium hydroxide) process resulted in white, highly oriented, microfibriller celluose with an average diameter around 5 µm.

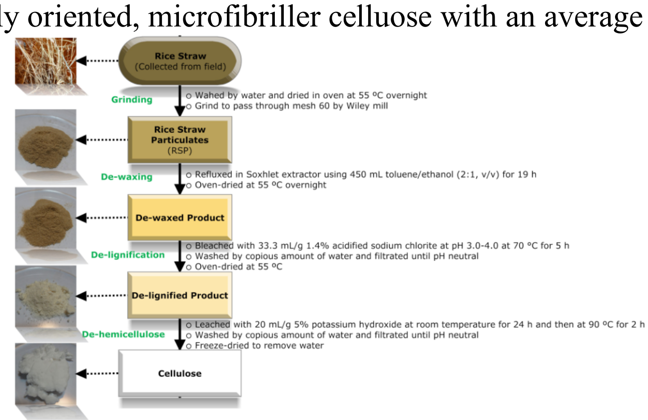

Figure 1. Isolation of cellulose

1b.1. Isolation of lignin and hemicellulose by sodium chlorite/potassium hydroxide process
This $NaClO_2$/KOH process removed lignin and hemicellulose consecutively, but could not completely remove lignin whose presence was evident as the brown color in the filtrates from both steps.

1b.2. Isolation of hemicellulose and lignin by alkaline peroxide process
This NaOH and H_2O_2 process removed hemicellulose and lignin consecutively, isolated yellowish cellulose (37.14% yield) that may be bleached with 1.4% $NaClO_2$. Additional hemicellulose (17.275% yield: 47% HC1 and 53% HC2)) and lignin (8.75% yield: 71% Lignin 1 and 29% Lignin 2) may be precipitated from the filtrates of the latter steps and effectively collected individually as well as together as mixtures by combining filtrates from several steps. This process shown in *Figure 2* is deemed optimal and versatile for fractionation of both cellulose and the non-cellulosics.

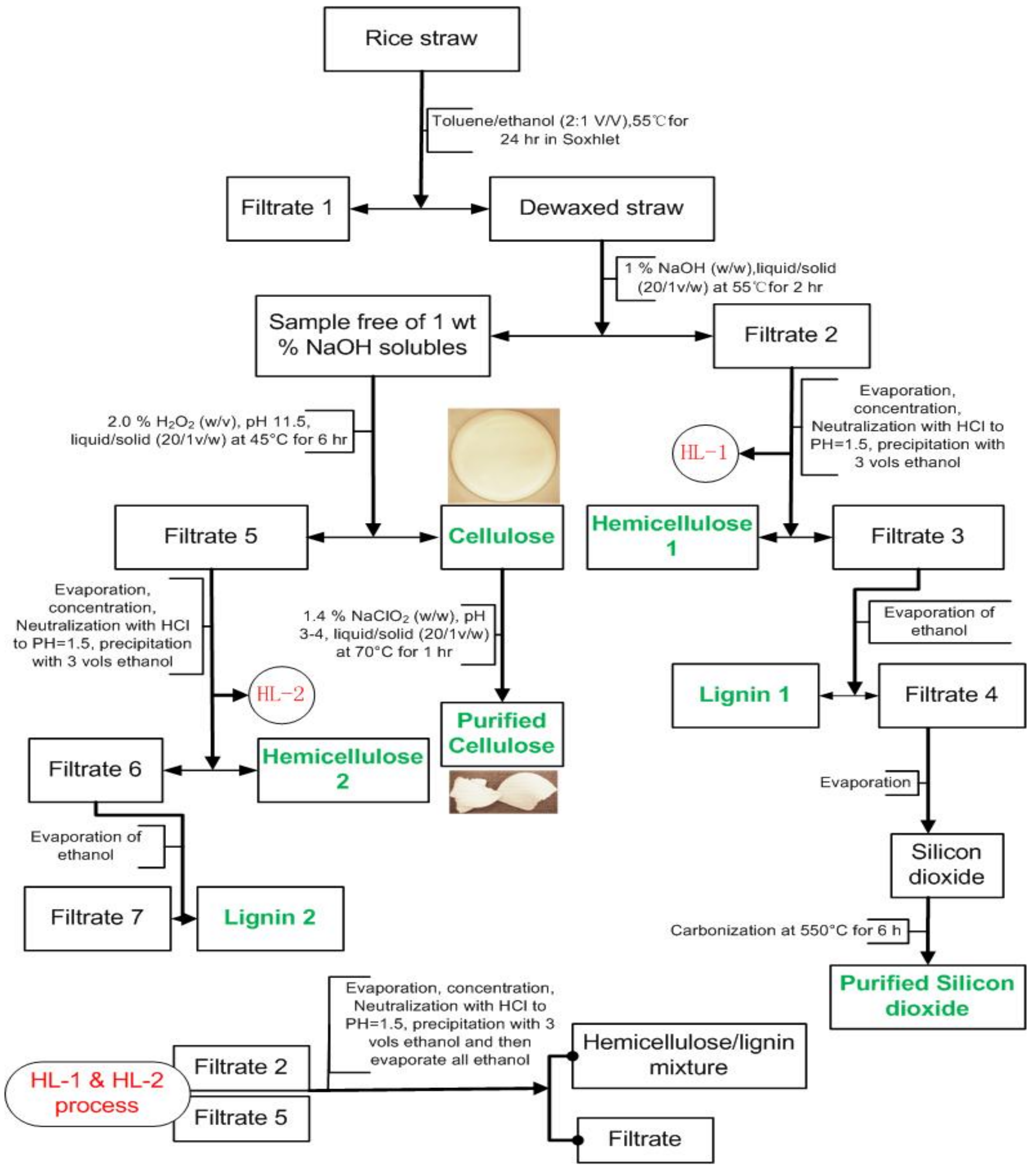

Figure 2. Isolation of hemicellulose, lignin and silica

Objective 2. Conversion of rice straw components

Of the proposed pathways, conversion has been achieved to varied degrees as indicated below:

a) cellulose nanocrystals (CNCs) – fully achieved
b) advanced cellulose nanofibers – fully achieved
c) porous carbon fibers and carbon nanofibers – initial evidence of carbon products
d) silicon carbide (SiC) nanowires – pure silica gel and silica nanoparticles are produced

Cellulose nanocrystals (CNC) in the forms of nanorods (less than 10 nm wide and 200 to 400 nm long) have been generated acid hydrolysis of rice straw cellulose. These CNC are narrower, but longer than those derived from cotton, i.e., higher aspect ratio, a distinctly superior feature. Similar acid hydrolysis and freeze-drying process for cotton cellulose will be adopted and developed for rice straw specifically. Toward products b, CNCs could self-assemble into ~300 nm diameter fibers with highly orientated organization along the fiber axes by a freeze-drying process. Furthermore, these self-assembled CNC fibers were highly stable under vigorous stirring or shaking in aqueous media and maintained their fiber morphology, showing great promise for processing into advanced materials including reinforcing fillers for green composite materials. Toward products c, we have recently established solution systems to produce nanofibers and fibrous membranes from industrial lignins and calcinated at 850^{o}C (submitted for presentation at the American Chemical Society meetings, Spring 2010).

For product d, thermal pyrolysis of rice straw led to 12.63% yield of white ash (*Figure 3a*). Alkaline extraction of silica produced silica gel upon neutralization. Removing water from silica gel led to silica nanoparticles (*Figure 3b*).

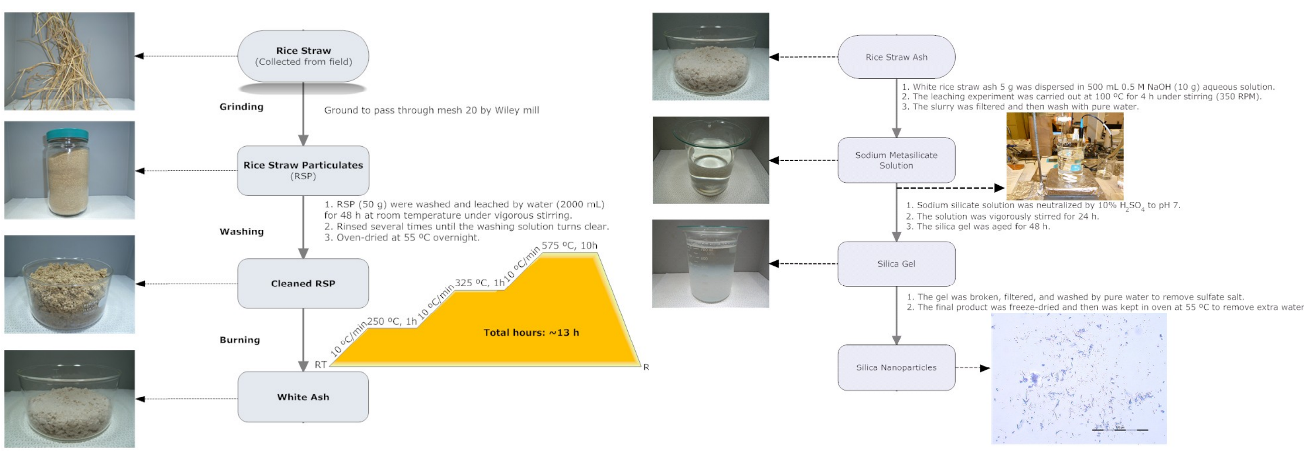

Figure 3. Pure silica, gel and nanoparticles from thermo-chemical processes

PUBLICATION:

A paper titled "Self-assembly of cellulose nanocrystals to cellulose ultra-fine fibers" has been submitted and accepted for an oral presentation at the American Chemical Society Spring Annual meetings in Anaheim, March 27-31, 2011.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

This project is to develop efficient strategies to separate (isolate/fractionate) rice straw components and to convert them to new advanced nano-materials and performance industrial products. Several chemical pathways have been evaluated and optimized to separate the major rice straw components, i.e., cellulose, hemicellulose, silica and lignin.

Two distinctively advantageous processes have been successfully demonstrated to: I) derive pure cellulose, and II) isolate hemicellulose, lignin and silica. Cellulose has been isolated by a number of ways. The optimal method to derive pure cellulose is a stream-lined three-step process involving acidified sodium chlorite and potassium hydroxide. The de-wax, de-lignification and de-hemicellulose steps yielding over 95%, 99% and 41%, respectively, produced at least 36% of pure cellulose. In a process using sodium hydroxide and hydrogen peroxide, hemicellulose, lignin and silicon can be effectively collected individually as well as mixtures by variations of this approach. Cellulose nanocrystals with diameters less than 10 nm and lengths ranging from 200 to 400 nm have been generated. Pure silica nanoparticles have been derived from thermal pyrolysis of rice straw followed by chemical extraction. Several isolation procedures have been evaluated and optimized to allow versatile and efficient pathways to generate any and all of the four major rice straw components at high yields.

The successful conversion of these rice straw components to cellulose nanocrystals, self-assembled fibrils, as well as silica gel and nanoparticles validates the proposed concepts and sets the foundation for further development of these nanomaterials for high value added industrial products.