IMPROVED SUPERABSORBENT KRAFT PULPS

GT Project Staff:

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PROJECT OBJECTIVE:

The objective of the proposed work is to provide a new technology for enhancing the water absorption properties of fully bleached softwood and hardwood kraft pulps by 20 – 50%. This goal will be accomplished by sulfonating the carbonyl groups that are present in all modern bleached kraft pulps. The results of this study will be a novel treatment for improving the water absorbency properties of tissue, towel and fluff pulp. These deliverables address Agenda 2020 and the Institute's strategic research vision which challenges researchers to develop "New Products-New Uses for Fibers." Support of this project will provide a viable alternative to petroleum derived super-absorbers may used in modern products.

PROJECT BACKGROUND

General Description: Cellulose is the most abundant and renewable biopolymer provided by nature and it is a key resource for the development innovative sustainable biomaterials.[1] Its chemistry and application is nowadays undergoing a renaissance, due in part, because of its applicable as a value added material with excellent life-cycle analysis properties.[2]

It has been well established that carboxyl groups of fibers influence several key physical properties of fibers including the swelling of wet fibers, fiber flexibility, fiber–fiber bonding, and refinability.[3,4,5] Increased fiber charge is frequently accomplished by oxidative conversion of cellulosic hydroxyl groups to carboxylic acid groups or other acidic groups. For example, hydrogen peroxide oxidation of ECF bleached kraft pulps increases the carboxylic acid content of cellulose.[6]

In the past fifty years, research in the field of superabsorbent products has developed rapidly because of an increasing demand for their applications in the personal care absorbent markets.[7] The term superabsorbents encompass a number of polymers, which all effectively absorb water, and are essentially hydrophilic cross-linked polymers that can absorb several hundred times their weight in water, but cannot dissolve because of their three-dimensional polymeric network structure. These super-absorbent materials have many applications including children and adult incontinence products, feminine hygiene products. They have also used in the oil drilling industry and for reducing soil erosion abetment. [8]

The production of superabsorbents for personal care covers almost 80% of the over all production of hydrogel production nowadays, and this attractive business has accelerated industrial and academia developments in this field.[9,10,11] Most current superabsorbents are non-biodegradable polymer-based products, the renewed public attention favoring environmentally benign products has encouraged the development of biodegradable superabsorbents based on cellulosic materials.[12,13]

Recently, we have demonstrated that the water absorbing properties of cellulose can be enhanced by oxidation and sulfonation to provide absorbent properties desirable for use in disposable absorbent products. This program will extended this approach to utilize the native carbonyl groups in bleached kraft pulp as sites for further sulfonation. It is anticipated this will provide a facile technology for enhancing the water absorbent properties of fully bleached kraft pulps.[14]

Recent Work

In our ongoing cellulose modification studies the copper numbers and total acid group of several series of cellulose samples were measured after the oxidation and sulfonation process, respectively.[14] We have observed that:

- There is a higher carbonyl group content increase after oxidation for all the cellulosic samples generally.
- Sulfonation increased the total acid group content (Table 1) and water retention properties of the treated pulps.

Entry	Total acid group (mmol/100 g o.d. fibers)
Cotton Cellulose Cu # = 0.68	2.00
Oxidation 1: Cu # = 5.11	1.87
Sulfonation of Oxidation 1	3.55
Oxidation 2: Cu # = 7.13	1.79
Sulfonation of Oxidation 2	5.90
ECF Bleached Birch Cu # = 0.46	6.56
Oxidation 1: Cu # = 4.29	5.08
Sulfonation of Oxidation 1	6.94
Oxidation 2: Cu # = 5.98	3.50
Sulfonation of Oxidation 2	7.21

Table 1. Copper number and total acid group measurements of various cellulosic samples. [8,14 §]

§ Note: Sulfonation was accomplished with sodium bisulfite. For these preliminary investigations the enhancement of the carbonyl content was accomplished with either 10 or 20% by mass periodate.

Preliminary water absorption results of our research indicated that the sulfonated cellulose possess higher water retention values as summarized in Figure 1.

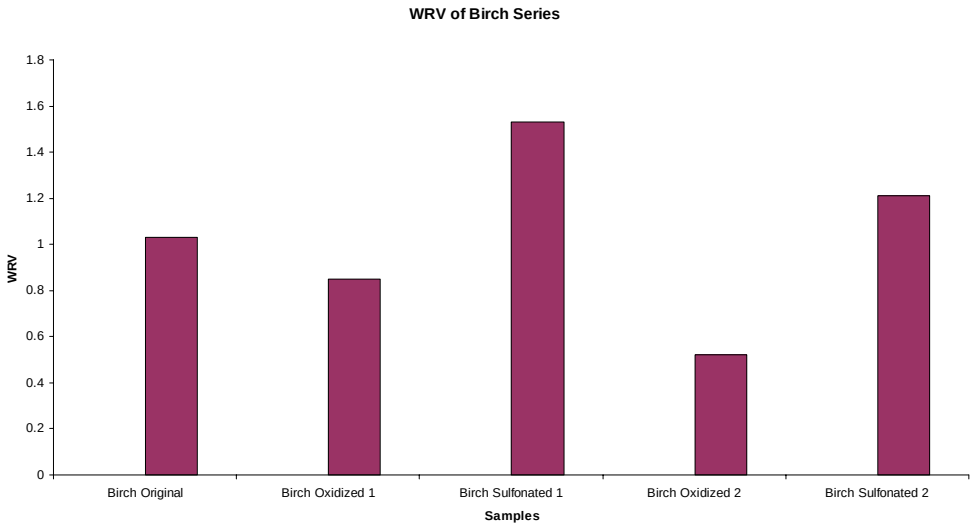

Figure 1. Water retention values (WRVs) of oxidized and sulfonated ECF bleached HW kraft pulp.

DESCRIPTION OF THE RESEARCH CONCEPT

PROGRAM DELIVERABLES:

We will delivery the following to our sponsors:

1. Optimizing reaction conditions (temperature, reagent ratio, etc.) for the sulfonation of fully bleached HW and SW kraft pulps from several commercial sources.

2. Determination of enhanced water absorption properties for sulfonated bleached kraft pulps.

3. Development of metal-assisted hydrogen peroxide stage to introduce additional carbonyl groups (i.e., increase Cu #) for subsequent sulfonation treatment.

VALUE OF DELIVERABLES:

This program is directed at pulp manufactures that need to develop enhanced water absorbency properties for bleached kraft pulps used for fluff, tissue and towel applications. The recent increase in petroleum prices has increased the cost of manufacturing synthetic superabsorbers which provides a unique opportunity to develop new cellulosic water absorbing materials. This exploratory project will develop a low capital/operating cost approach to address this challenge.

PROJECT GOALS:

This program is directed at enhancing the water absorbent properties of ECF bleached pulps by a factor of 40% or greater.

PROGRAM APPROACH:

Task 1: Sulfonation of Bleached Kraft Pulps from Various Sources.

Initial research studies will develop optimal sulfonation conditions (i.e., sodium bisulfite) to react fully with all the carbonyl groups in commercial bleached kraft pulps. The degree of oxidation and sulfonation will be increased by the use of a modified peroxide stage (i.e., H_2O_2 in the presence of metals such as Ni, Cu, Mn) and followed by sulfonation with sodium bisulfite. This treatment will be optimized according to reaction temperature, time, pH and stoichiometric amounts of reagents employed.

Task 2. Measurement of Pulp Cu # of the oxidized cellulose and Acid Groups of Sulfonated Cellulose.

In parallel with Task 1, the contents of carbonyl groups of the oxidized cellulose will be determined by measuring the copper number, and the total acid groups of the sulfonated cellulose will also be determined by titration.

Task 3. Evaluation and Screening of Cellulosic based Superabsorbents.

In parallel with Task 1 and 2, the treated pulps will be evaluated for their water retention values (WRVs), other factors such as their transformation yield, reagents consumption, etc., will also be taken into consideration for the optimization of the consideration superabsorbent screening.

Task 4. Investigation of the relationship between the absorbent properties and their chem.-physical properties, morphologies and structures.

In parallel with all the previous tasks, it is necessary to study the depolymerization of cellulose after oxidative modification which will be assessed by determining the intrinsic viscosity of the treated pulps. Different instrumentations such as Fiber Quality Analysis (FQA), FT-IR, Solid ^{13}C-CP/MAS NMR, and AFM will be applied to study the relationship between the absorbent properties and their chemi-physical properties for the development of improved superabsorbents based on modified cellulosic materials.

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