Simplified Pulping and Bleaching of Corn Stalks

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Abstract

A simplified 3 to 4 stage process has been developed to produce fully-bleached pulps from corn stalks. The process consists of a mild alkaline extraction, followed by acidification, ozonation, and final bleaching. The ozone stage serves as a chemical depithing stage and permits free-draining pulps to be produced without mechanical depithing. In this paper, preliminary data are shown for trails on US corn stalks. Strength properties of handsheets from corn stalks pulps were compared to those for southern hardwoods.

Dr. Byrd and Mr. Hurter were granted United States Patent 6,302,997 - Process for producing a pulp suitable for papermaking from nonwood fibrous materials (2001) for this process. Patent protection is being processed for the European Union, Canada, Mexico, India, China and other countries.

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OUTLINE

- Why Cornstalks?
- Why *NOT* Cornstalks?
- Our experiences with cornstalk pulping
- A new approach
- Experimental
- Process Results
- PFI Refining and Handsheet Testing
- Additional Work

WHY CORNSTALKS?

1. Why Nonwoods?

- Trees….available for the future?
- Trees…more valuable for other uses?
- Regional shortages of hardwoods
- Consumer demand for “tree-free” paper

2. It’s an Agricultural Residue

- Grain pays for growing costs
- Source of extra income for farmer

3. Lots of It Available

Residue Type	U.S. Availability, OD tons/year
Corn stalks	300,800,000
Wheat straw	78,900,000
Barley straw	12,000,000
Sorghum straw	12,000,000
Rice straw	7,500,000

Rowell and Cook, 1998 N. American Nonwood Fiber Symposium

4. Physical/Chemical Composition

	Cornstalks	Hardwoods
Fiber length, mm	1-1.5	0.7-1.6
Fiber diameter, microns	20	20-40
Lignin content, %	15-18	23-30
Cellulose content, %	44-47	38-49

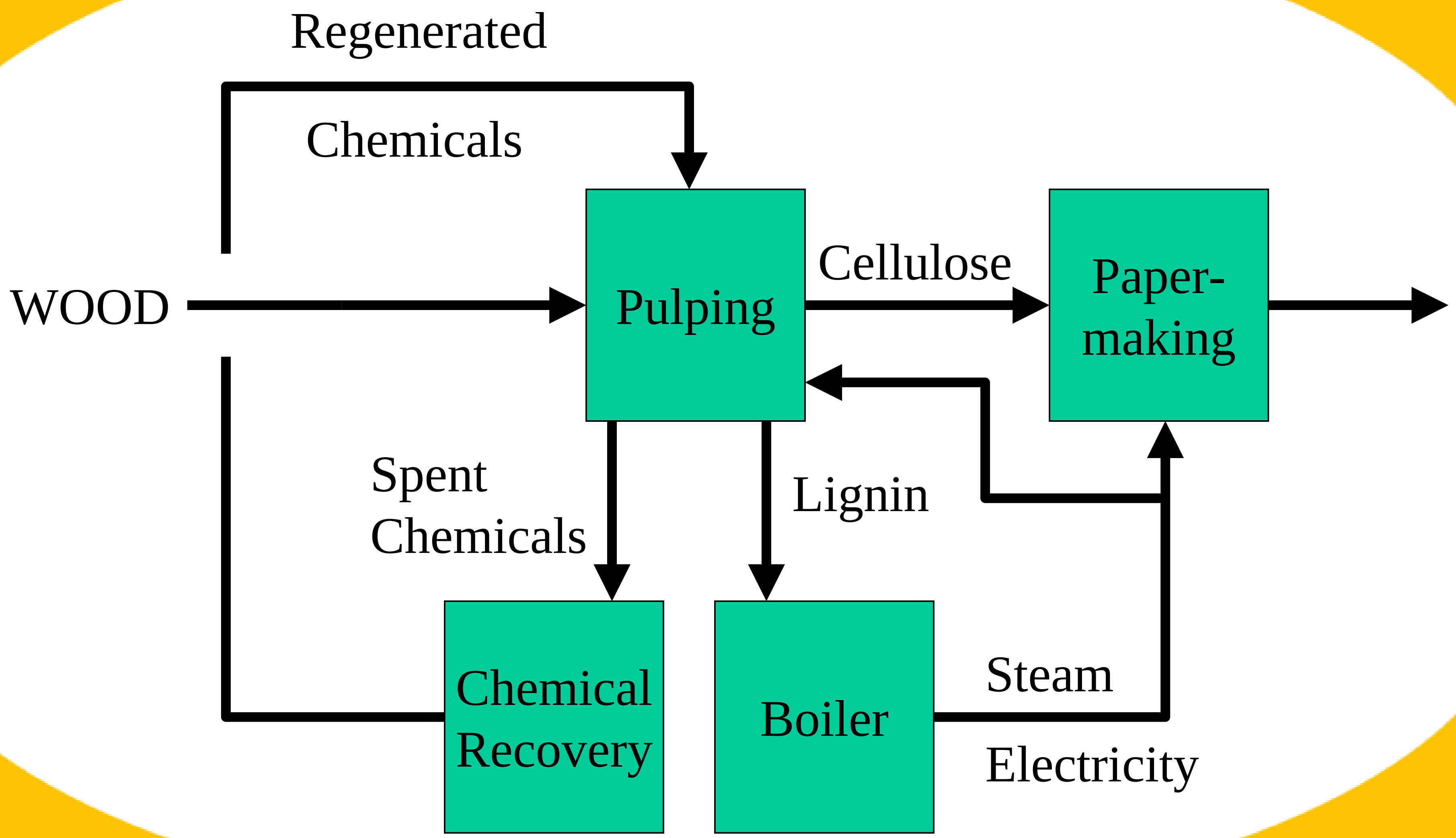
>Atchison, Pulp and Paper Manufacture, Vol. 3
>Eroglu, 1992 TAPPI Pulping Conference, Book 1

Why *NOT* Cornstalks?

1. Trees and Wood

- Wood is a *good* fiber supply for papermaking
- Forest growth in the US exceeds harvests by 37 %
- Wood has a clean, uniform composition --with few contaminants, and fibers well-suited for papermaking
- The wood-based pulping and bleaching process is very, very well-balanced – at least at large scale

A DAMN GOOD SYSTEM



2. The Challenges of Annual Crops

- Must harvest at one time and store all year
- Susceptibility to pests, fire, disasters
- Cost volatility?

3. The Challenges of Corn Stalks

- Low bulk density – storage, transport costs
- Can’t process in wood-based equipment
- Modest fiber quality
- Silica (?)

4. Extraneous Materials

- High content of pith – parenchyma and fines
- Poor drainage, high chemical consumption
- Requires de-pithing prior to pulping

What is Needed to Make Cornstalk Pulping Work

- A simplified process that lends itself to "mini-mills" located in the supply area
- A process that deals with pith without expensive mechanical de-pithing
- A process that preserves drainage rate

Our Experiences in Pulping Non-Depithed Cornstalks, With TCF Bleaching

1. Soda Pulping with TCF Bleaching

	Brightness, % ISO	**Freeness, CSF**
Pulping, 20 % NaOH, 140 C, 90 minutes	25-30	400-450
Bleaching, Q-P-P	68-75	350-400
Bleaching, Q-Pp-P	82-84	280-360
Bleaching, Q-Pp-Q-P	**84-88**	**270-300**

2. Soda-AQ Pulping with TCF Bleaching

	Brightness, % ISO	**Freeness, CSF**
Pulping, 11 % NaOH, 0.1 % AQ, 140 C, 60 minutes	14-25	360-423
Bleaching, Q-P-P	**78-82**	**280-332**

The Deficiencies

- “Traditional” pulping and bleaching approaches do not remove or passivate pith
- The pith breaks up in the bleaching sequence (especially acid stages), reducing freeness significantly

A New Approach --
The E-A-Z-P Process...
US Patent Number 6,302,997

Attributes

- A simple, 2- or 3-stage process (3- or 4-stage including screening)
- Requires no raw material depithing
- Produces bright, free-draining pulp with good papermaking properties

Two Key Concepts

- ***Lowered pulping intensity*** – many processes tend to “overcook” cereal straws, actually reducing lignin removal
- ***In-process treatment of pith*** – deals with pith and parenchyma chemically in the process, rather than using mechanical depithing of the raw material

E – Alkaline Extraction

- Milder than a typical soda or soda-AQ cook
- Typical conditions
  - NaOH charge = 12-14 % on OD
  - Temperature = 115-118 C
  - Time = 60 minutes
  - Liquor:Fiber = 8:1
- Kappa = 18-20

A - Acid Chelation

- Can use nitric, sulfuric, or acetic acids
- Typical conditions
  - Acid charge = 5 % on OD
  - DTPA (chelant) charge = 0.5 % on OD
  - Consistency = 10-15 %
  - Temperature = 60 C
  - Time = 30-60 minutes

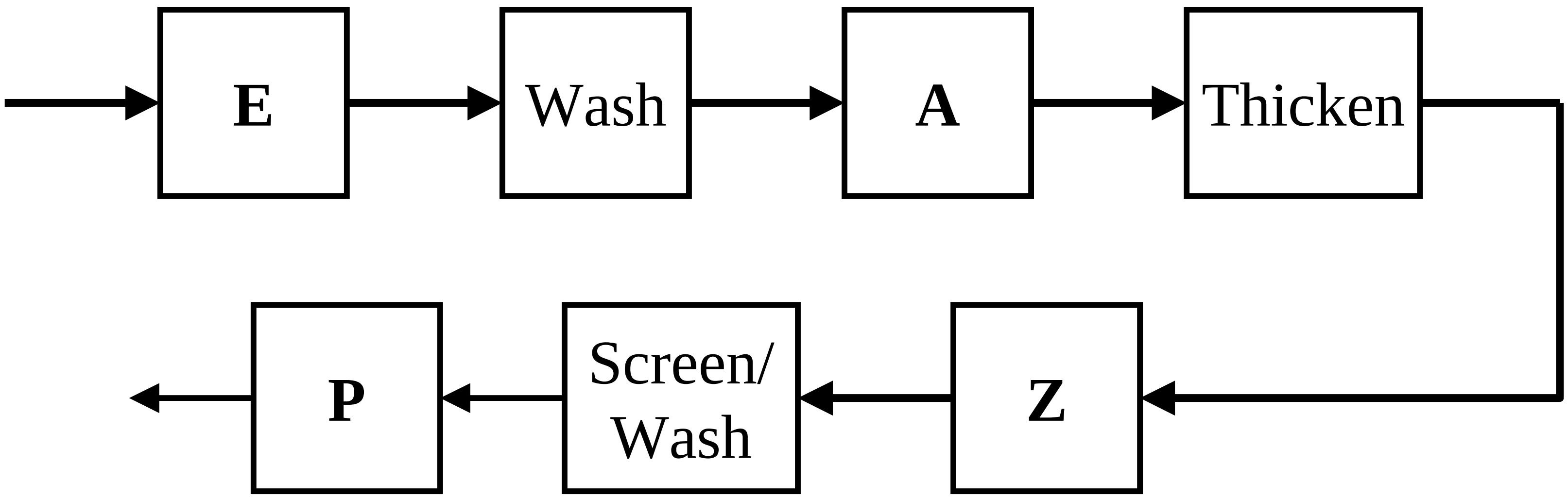
Z – Ozone Treatment

- Typical conditions
  - Ozone consumption = 0.7 – 1 % on OD
  - Consistency = 3 %
  - pH = 1.5
  - Temperature = 30 C
  - Time = 10 minutes

P = Pressurized Peroxide Bleaching

- Typical conditions
  - Peroxide charge = 4 % on OD
  - NaOH charge = 5 % on OD
  - DTMPA (chelant) charge = 0.2 % on OD
  - $MgSO_4$ and Silicate charge = 0.5 % on OD
  - Consistency = 10-12 %
  - Temperature = 105 C
  - Time = 90 minutes

Basic Process Flowsheet



Experimental Methods

Raw Material

- Corn stover from Iowa, aged 1 year
- Composition = 70 % stalk, 30 % leaves and husks
- Prior to pulping, soaked in hot water (130 F) for 30 minutes, then drained

E Stage

- Carried out in Paprican-designed “finger reactor”
- Good for emulating screw-type digester
- Cooked fiber passed through disk refiner, 0.035-inch gap
- Washed

A Stage

- Carried out in sealed plastic bags placed into a heated water bath
- Nitric acid used
- Kneaded periodically

Dewatering Stage

- Acid-treated fiber centrifuged in fine-mesh poly bag for 5 minutes
- Discharge consistency = 35 %
- Z stage followed immediately

Z Stage

- Centrifuged pulp diluted to 3 % consistency with distilled water
- Acid added
- Put into modified blender with non-cutting rotor and gas sparger into mixing zone
- Ozone gas of known flow rate and concentration injected into blender; excess taken off top and bubbled into kill solution
- Reacted for 10 minutes

Screening/Washing Stage

- Z stage pulp diluted with distilled water to approximately 0.5 % consistency
- Screened through vibrating flat screen with 0.010-inch slot
- Accepts dewatered to 35 % consistency

P Stage

- Carried out in 3-liter bombs placed into heated oven on rotating rack
- Chemicals mixed in using industrial-style kitchen mixer

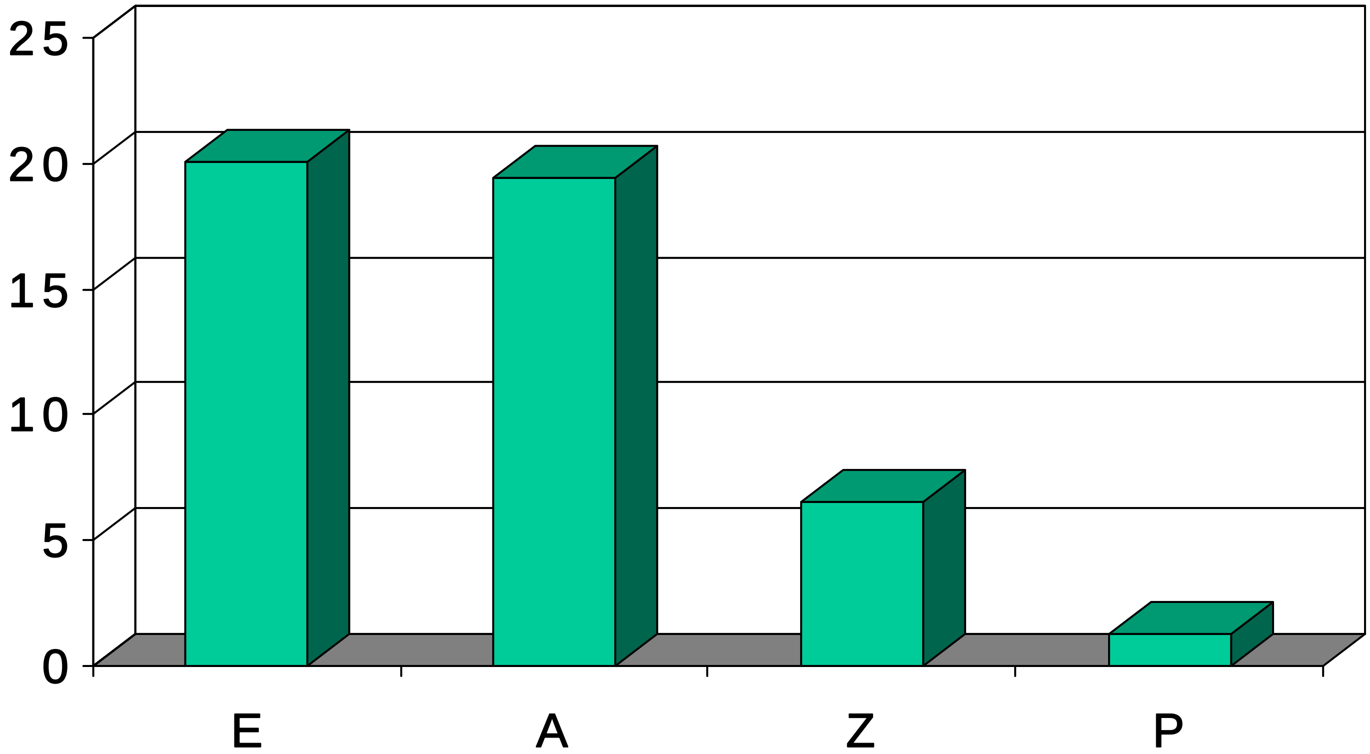
Process Results

Results by Stage

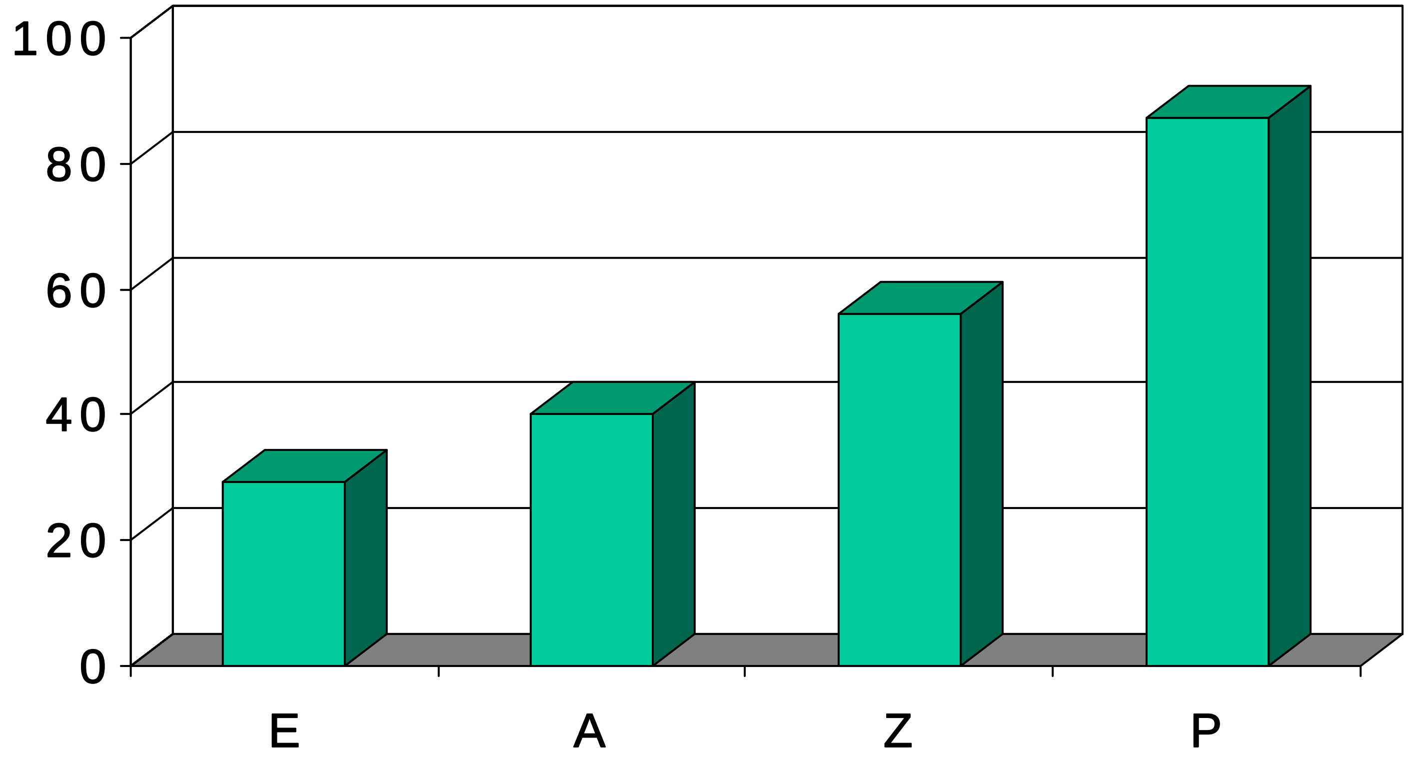
	Kappa	**Brightness % ISO**	**Freeness CSF**	**% Yield**
E	20.1	29.2	---	57.9
A	19.4	40.2	---	94.7
Z	6.5	56.1	587	**75.3**
Screening	---	---	---	98.7
P	1.3	**87.4**	**619**	93.2

Overall Yield = 38.0 %

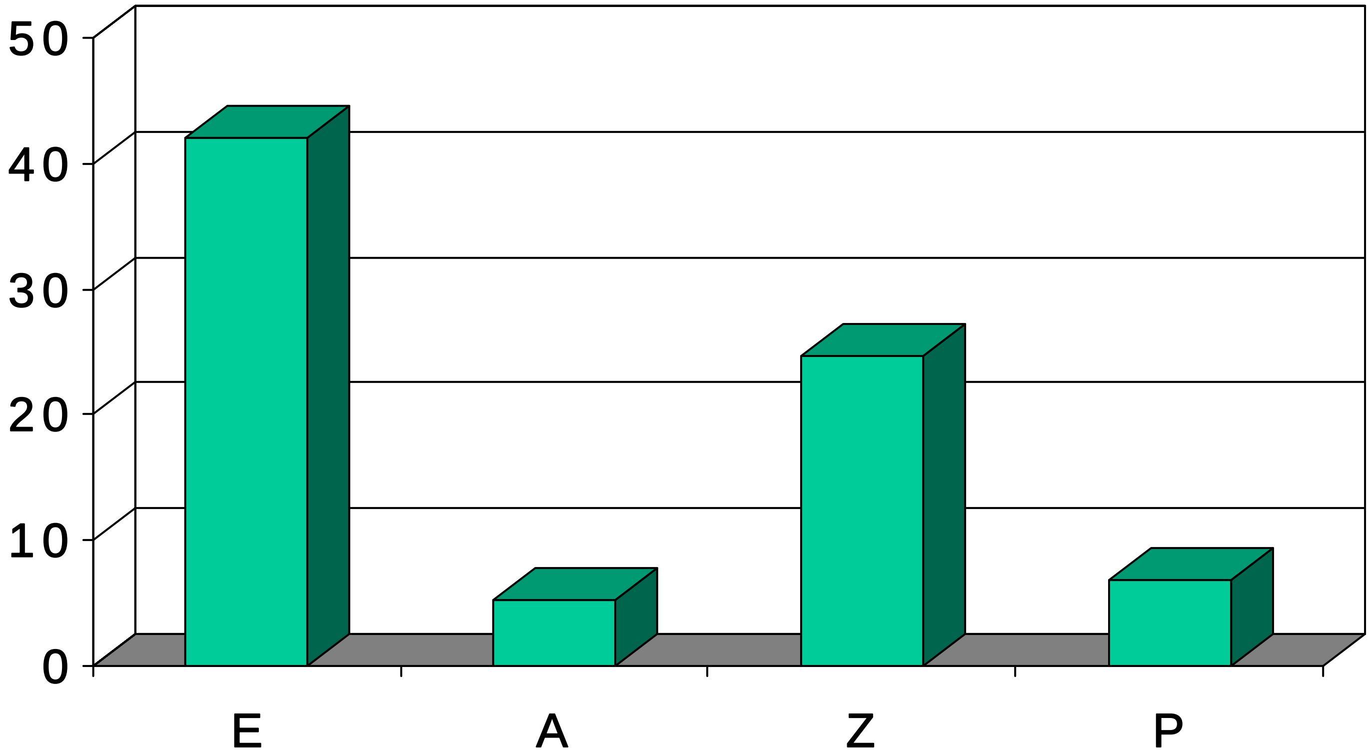
Kappa Reduction



Brightness Development



Yield Losses per Stage

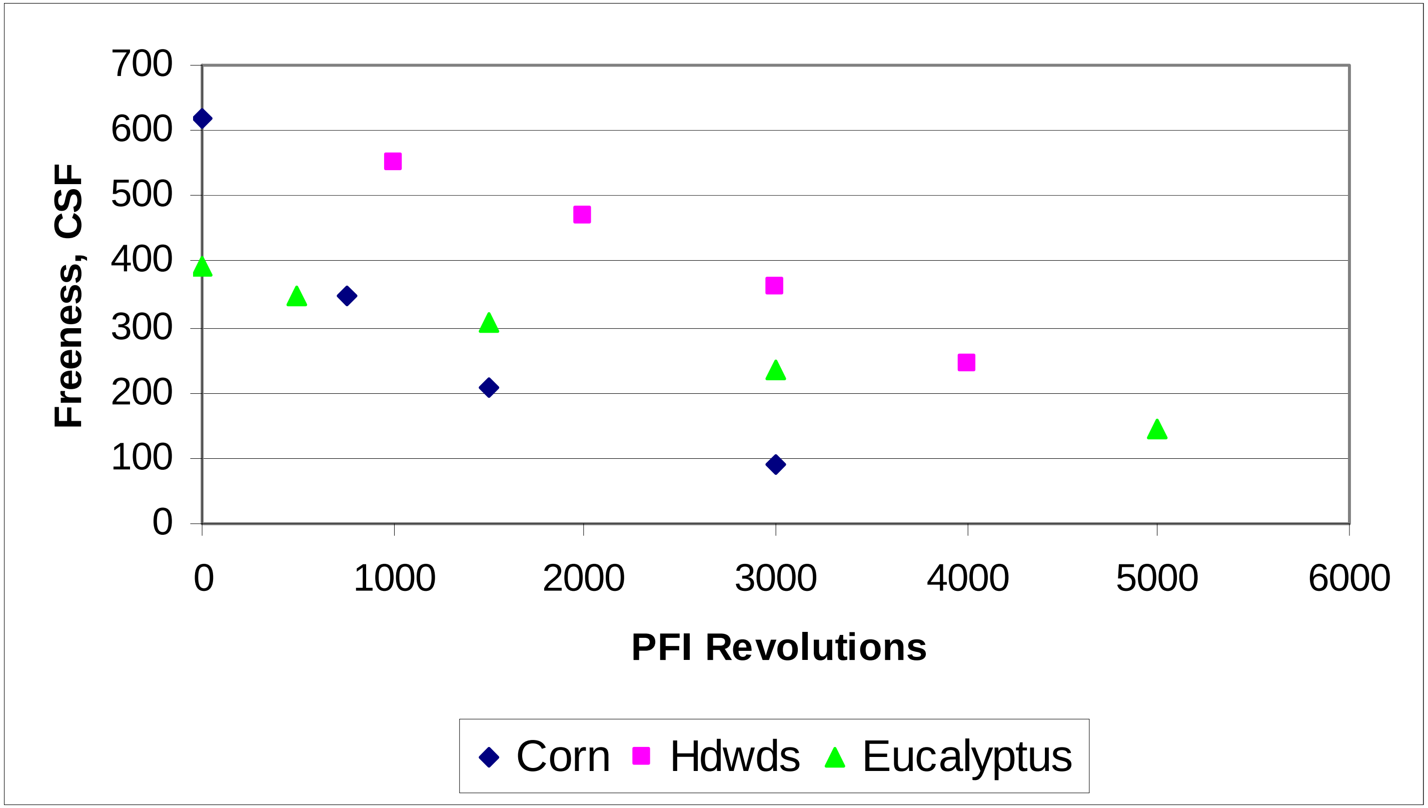


Bleached Fiber Properties

	Cornstalk	Mixed Hardwoods	Eucalyptus
Avg. Length, mm (Length-wtd)	1.09	1-1.07	0.65
Coarseness, mg/10m	1.06	1.23	0.95
Fines, % of total fibers (by number)	41.3	57.8	---

PFI Refining and Handsheet Testing

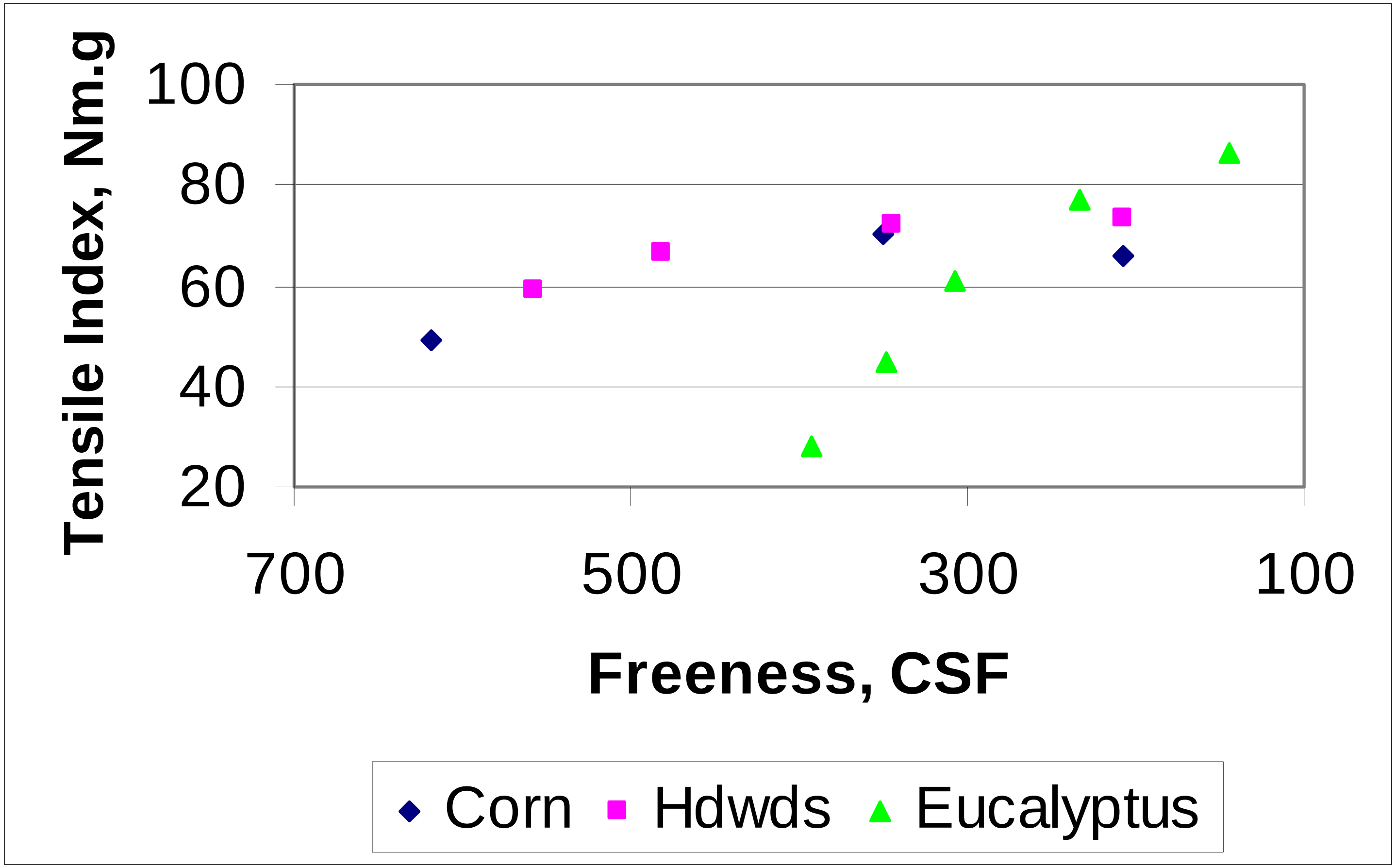
Refining Response



>Hdwds = NCSU kraft study data, mixed southern hardwoods

> Eucalyptus = N.I.S.T. data, Study 8496

Tensile Strength



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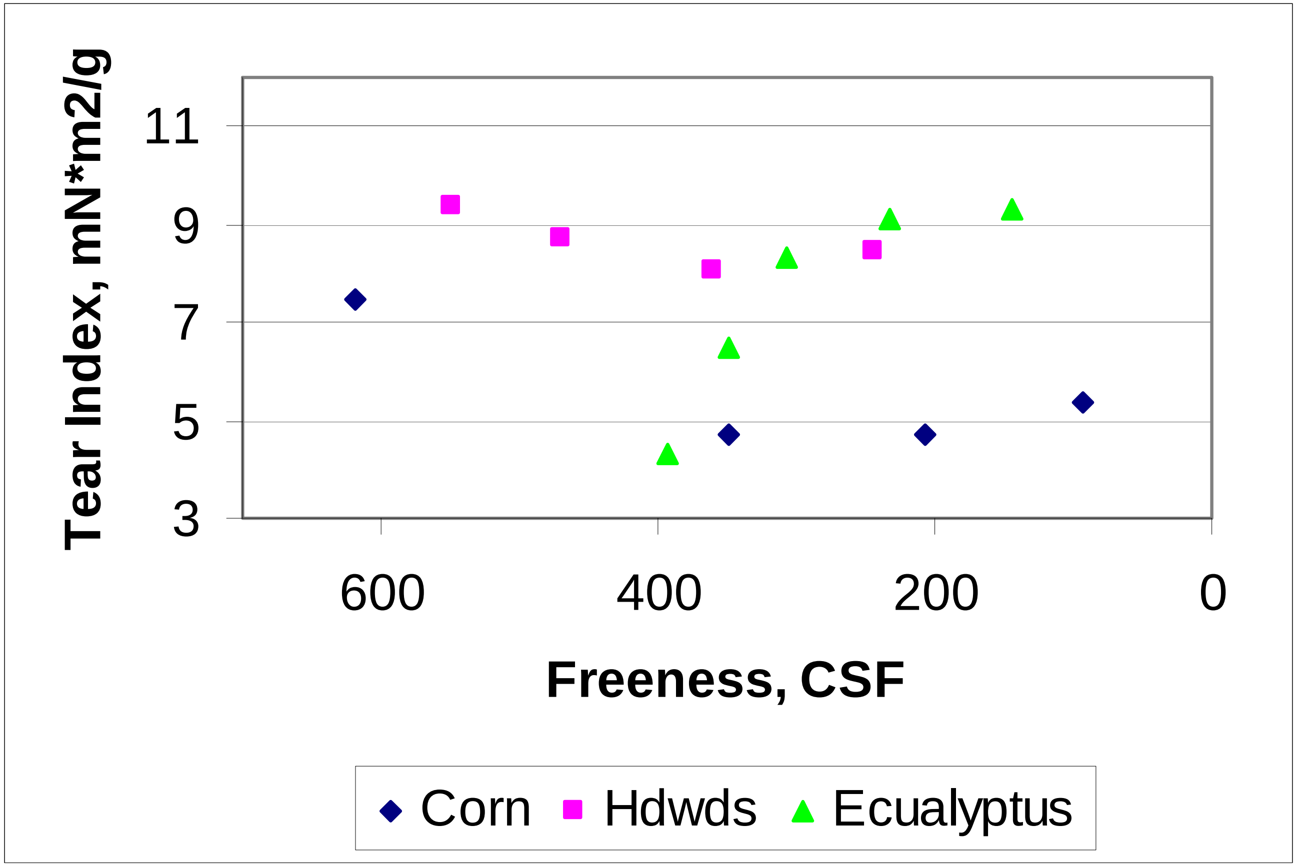
Tearing Strength



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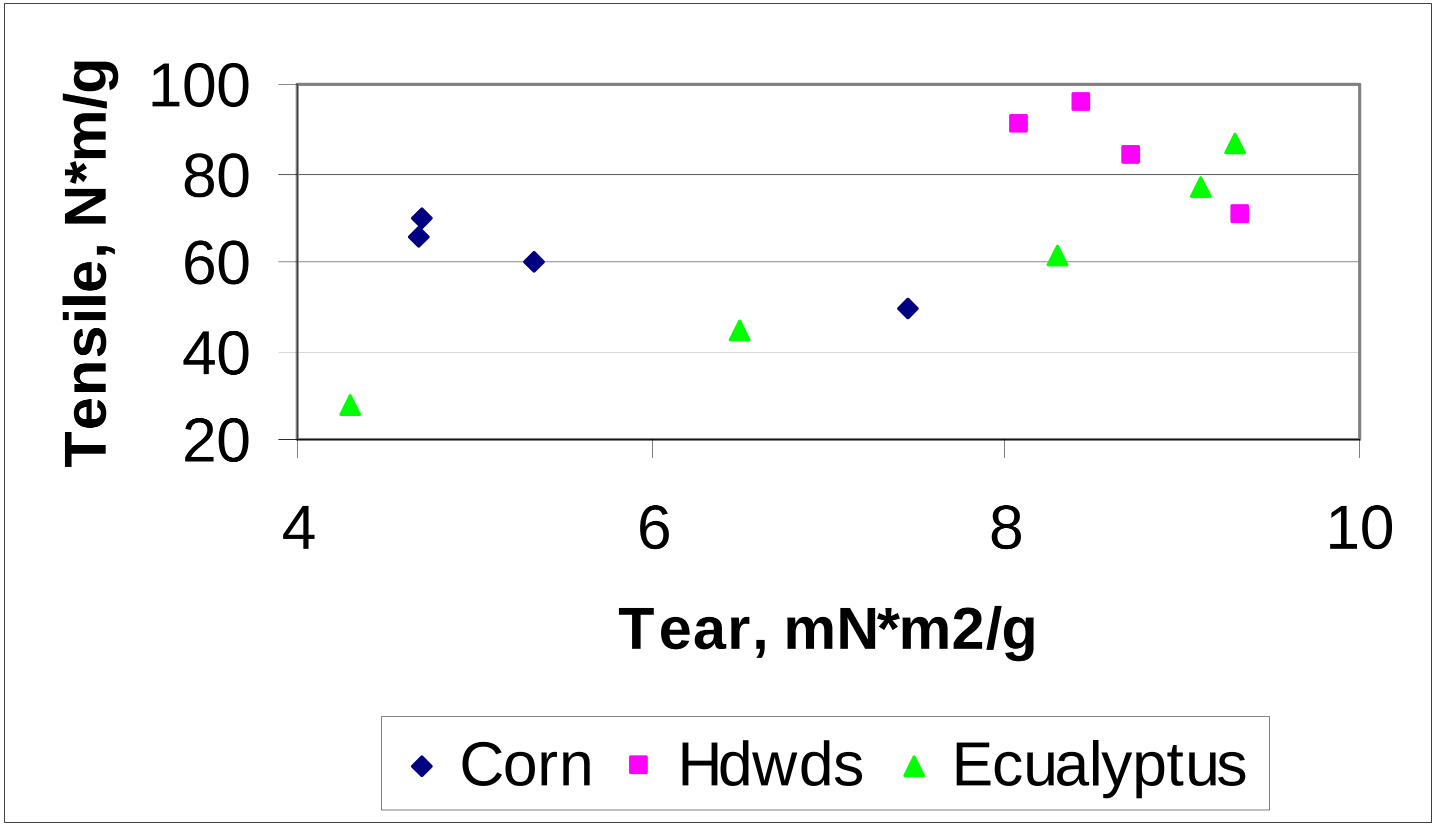
Tensile vs. Tear



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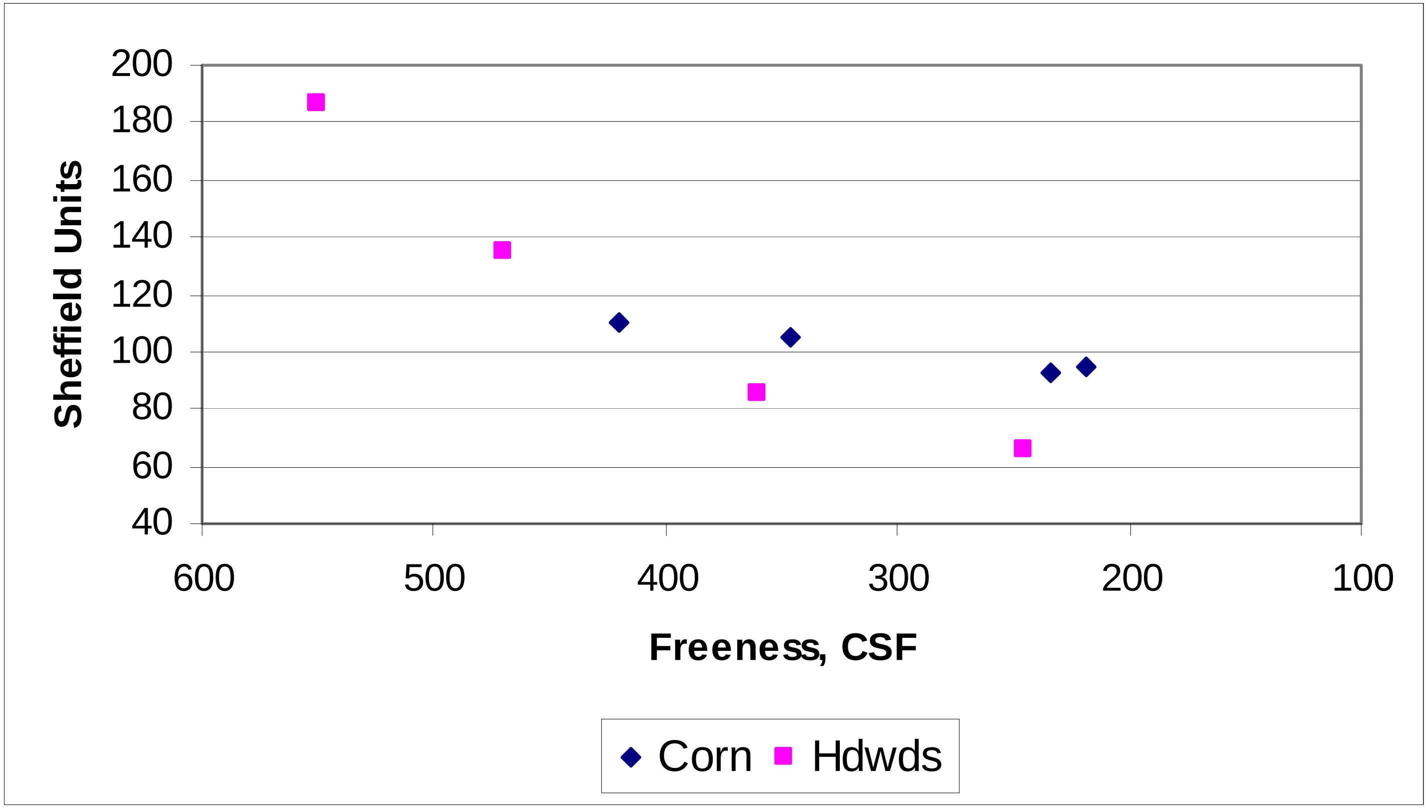
Smoothness



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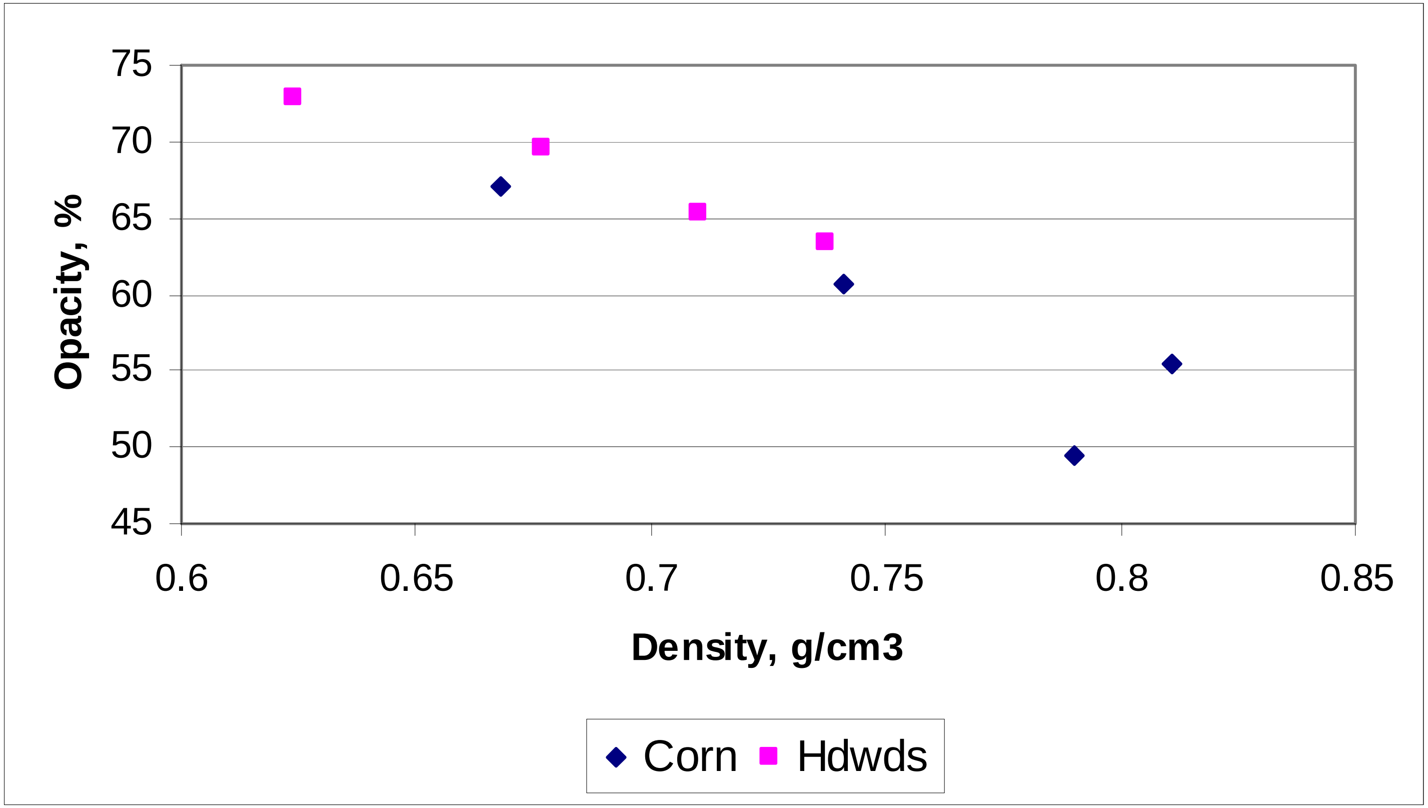
Opacity (Printing)



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Additional Work

Additional Work Completed

- Process works equally well with nitric, sulfuric, acetic acid
- Process works well with multiple alkali sources
- The chelant may be added into the Z stage, reducing the process to E-Z-P
- A D stage may be used instead of P

Ongoing Work

- Use of self-generated acetic acid from a pre-hydrolysis stage in the A or Z stage
- Effect of stover pre-treatment (e.g. shredding) on process results
- Application of process to other pithy nonwoods -- bagasse