

Modification of Medium Density Fiberboard Furnish: Analysis and Products

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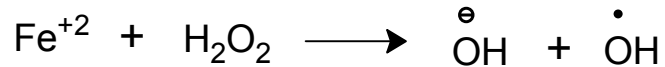


Fiber Modification

- Chemical
 - Oxidation with Fenton reagent
 - Nitric acid, potassium ferricyanide, sodium dichromate
- Enzymatic
 - Oxidation catalyzed by laccase
- Physical
 - Thermal
 - Ultrasound
 - Plasma

Chemical Modification

- Fenton chemistry



- Petri Widsten et al.

- Manufacture of Fiberboard from Wood Fibers Activated with Fentons Reagent ($\text{H}_2\text{O}_2/\text{FeSO}_4$).
Holzforschung 57:447-452

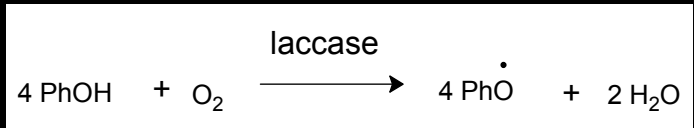
- Ulla Westermarck-12th ISWPC (2003)

- Nitric acid, potassium ferricyanide, sodium dichromate

- Johns and co-workers, Phillipou

- mostly on flakes

Laccase catalyzed oxidation



- Claus Felby and co-workers
 - Enhanced auto adhesion of wood fibers using phenol oxidases. *Holzforschung* 51: 281-286

Physical Modification Methods

- Physical modification
 - Processing changes
 - Thermal treatment
 - Plasma
 - Ultrasound
- These do not generate wastes, that require subsequent treatment and disposal

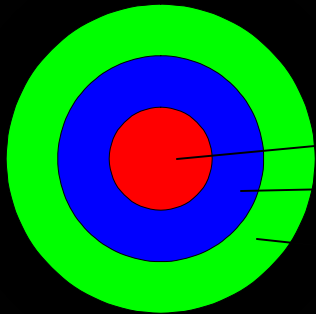
Processing Changes

- Maybe the simplest way to modify fibers is through changes in the processing conditions
- A large comprehensive study of chips refined over a large pressure range (2-18 bar) was initiated

Fiber Furnish



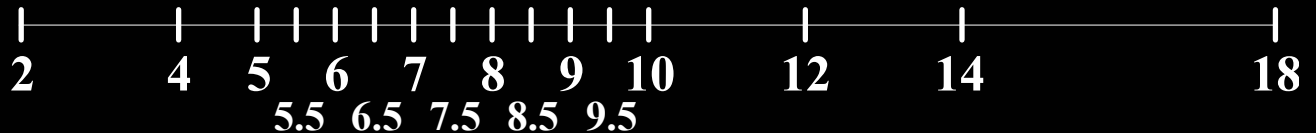
Juvenility and Refining



Juvenile = Rings 1 – 8
JuvTrans = Rings 9 - 16
MatTrans = Rings 17-24
Mature = Rings 24+



Refine at 16 different pressures at theBioComp Centre



Methods

- Fiber analysis
 - Single fiber mechanical properties
 - Near infrared
 - Wet chemistry
 - X-ray crystallography
 - Inverse gas chromatography
 - Time domain-Nuclear Magnetic Resonance spectroscopy

Time Domain-NMR

- Bruker minispec mq20
- Low field proton NMR (20 MHz)
- Relaxation times of protons
 - Free induction decay
 - T1 (spin-lattice)
 - T2 (spin-spin)



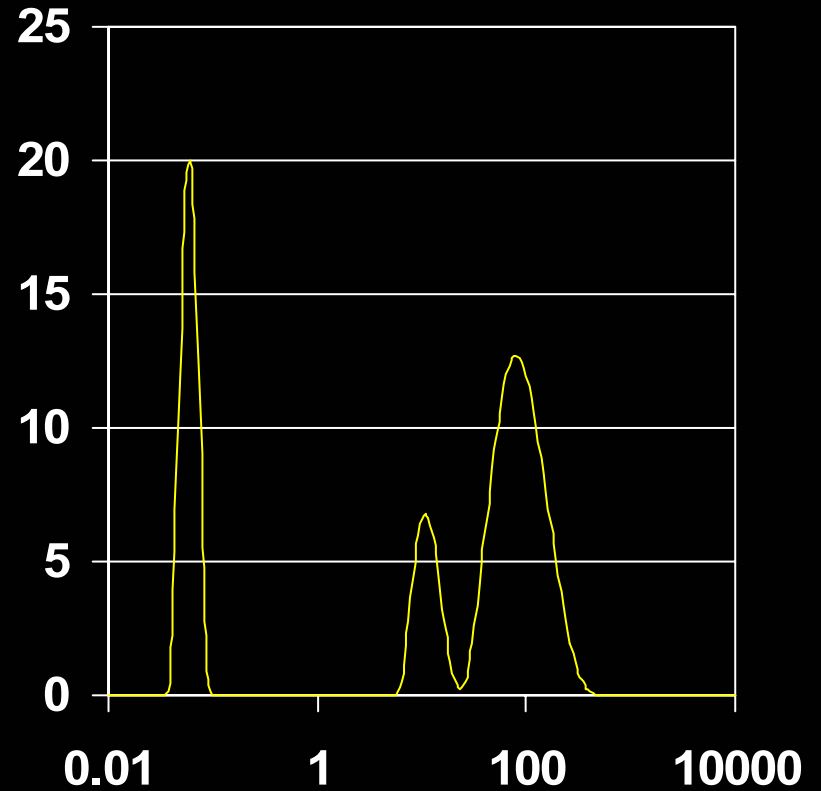
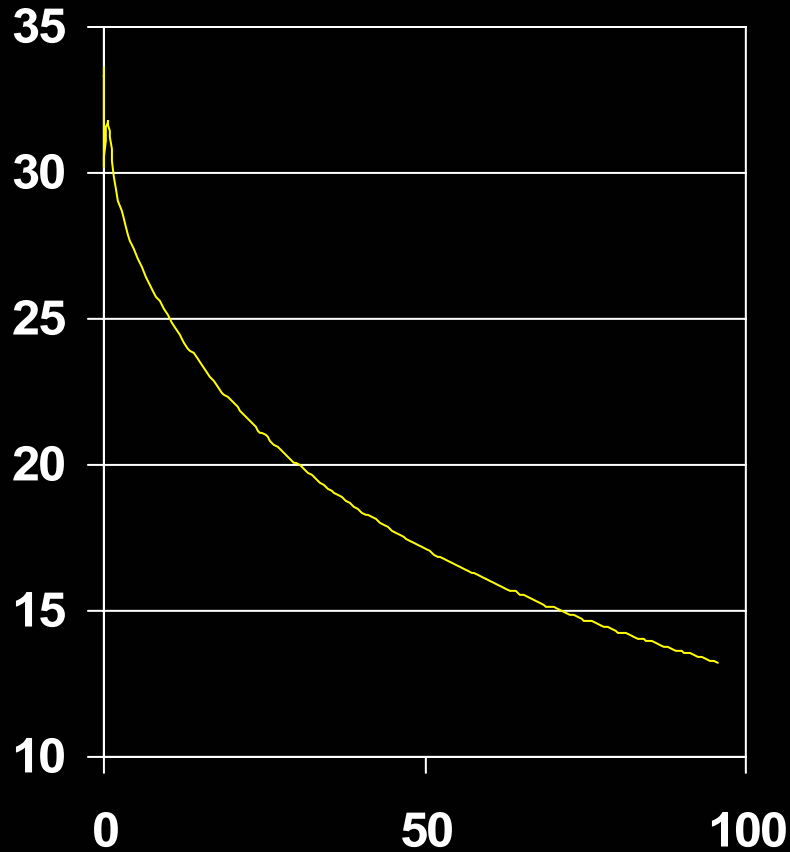
Time Domain-NMR

- Applications to wood
 - These methods have been used to determine the moisture content of wood
 - The nature of bound and free water
 - Differences in relaxation times can reflect impact of processing conditions on wood and wood fibers.

Methods

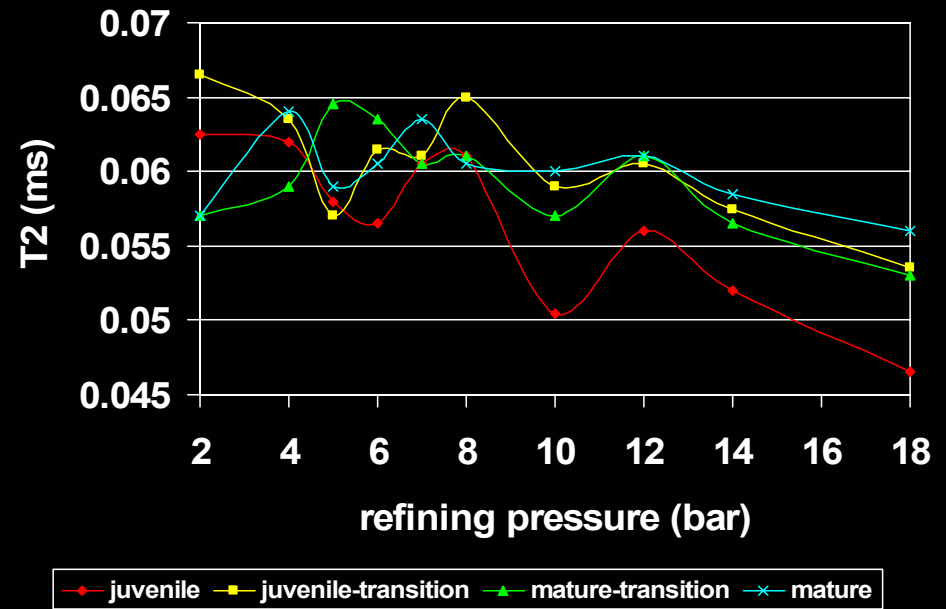
- Approximately 0.25g of each fiber type was weighed into 18mm test tubes and 1 gram of water was added to each tube. The fibers were equilibrated for seven days over distilled water in a dessicator at room temperature, such that the moisture content in excess of the fiber saturation point.
- Bruker FID_CP_MB pulse sequence
 - This is a standard Carr-Purcell-Meiboom-Gill method, but with the acquisition of an initial free induction decay in order to detect rapidly relaxing components
- $\tau=0.15\text{ms}$, time delay=5 seconds, 32 scans, with the acquisition of 256 echoes.
- The exponential magnetization decay was analyzed using Contin, which fits the curve using a Laplacian transformation as described by Provencher (1982), to provide a distribution of relaxation times.

Typical NMR Results



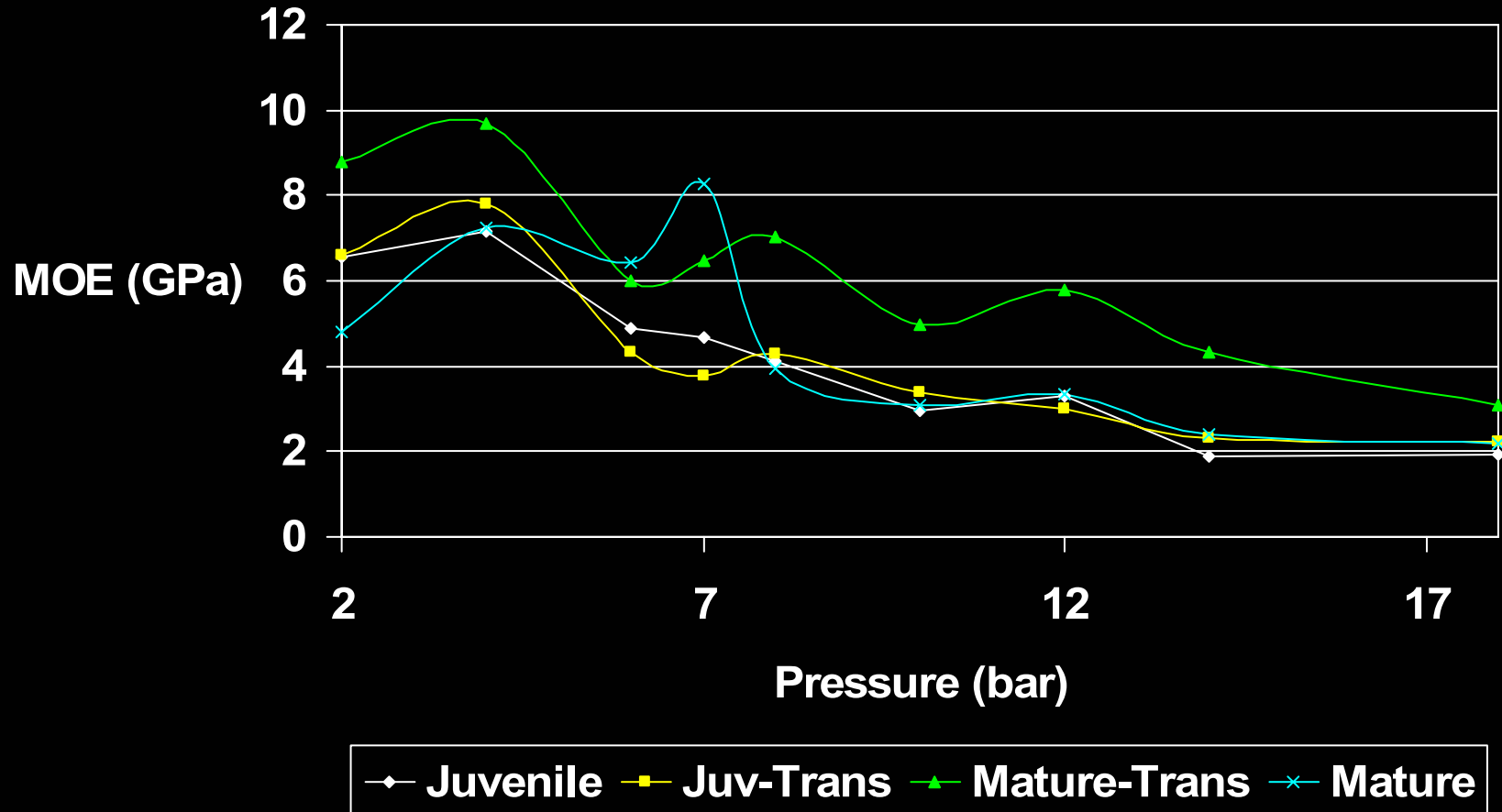
Results

- The relaxation times are variable but a general decrease in the shortest T2 was observed with refining pressure.
- The other relaxation times showed no particular patterns with respect to pressure.



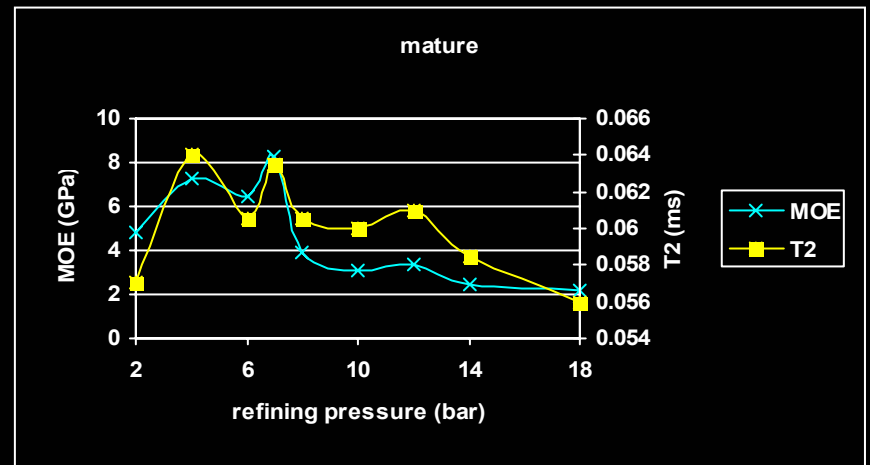
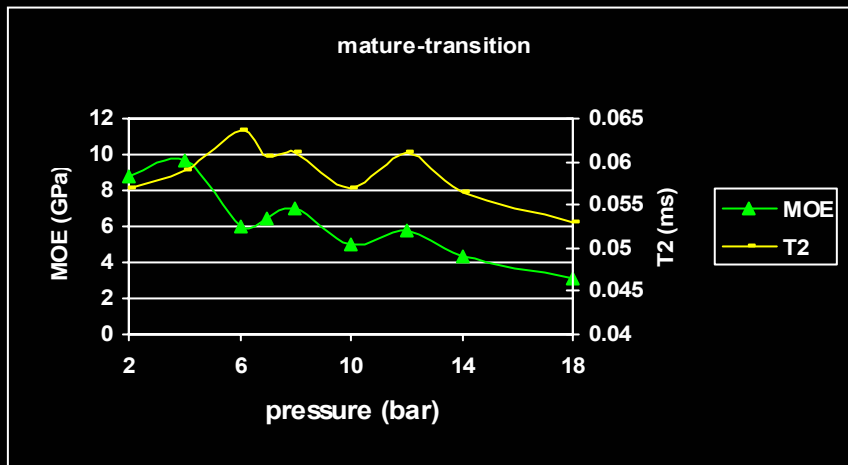
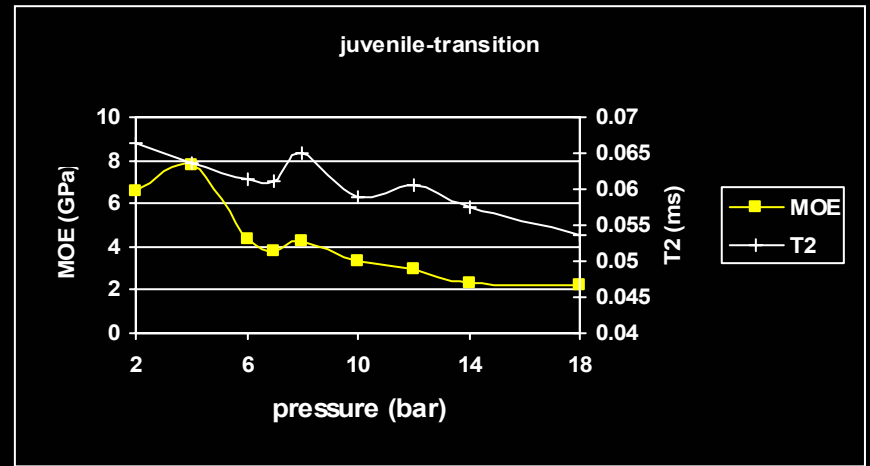
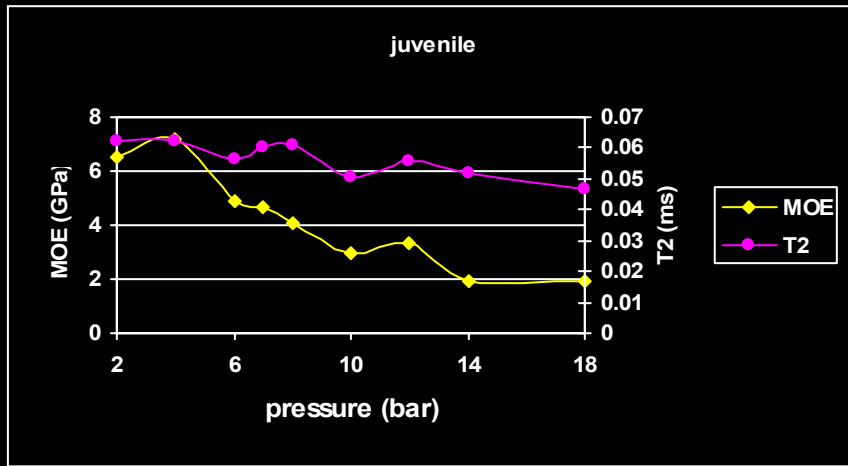
Results

Mechanical Properties



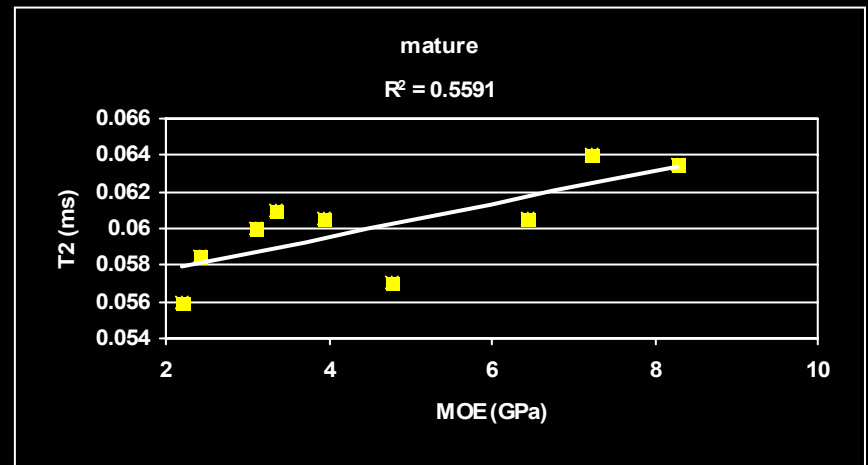
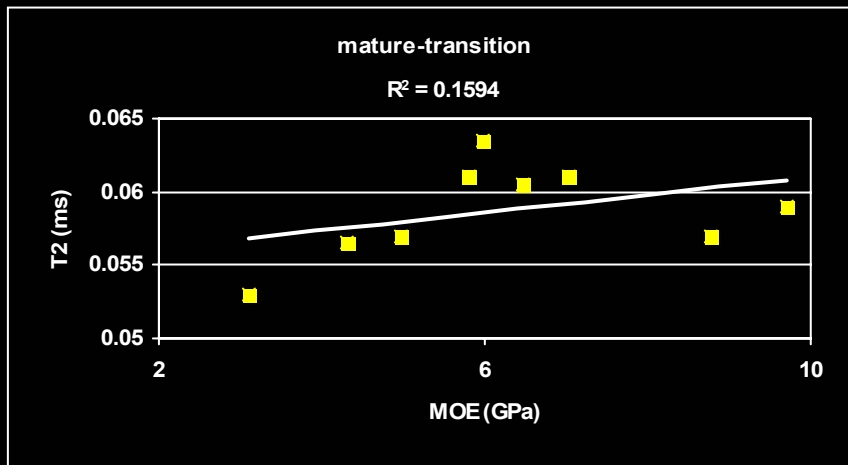
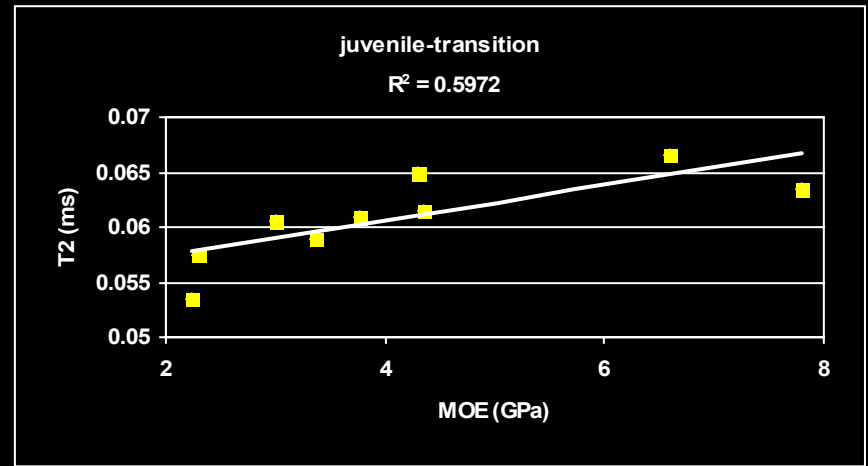
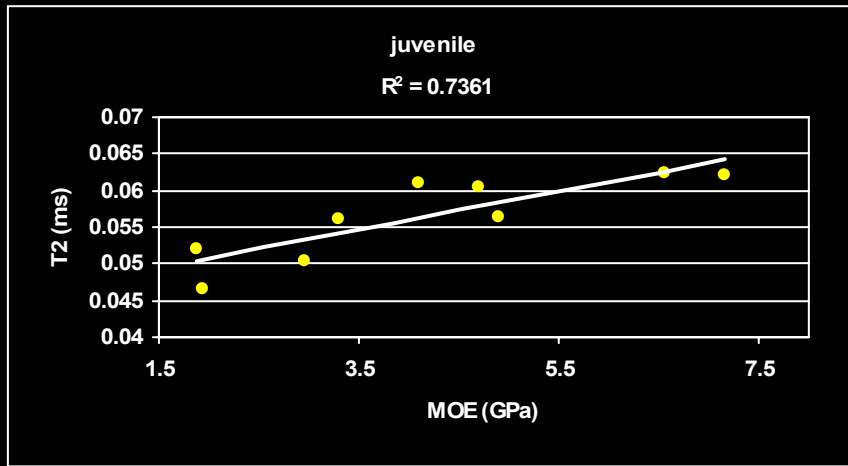
Results

Mechanical Properties/T2

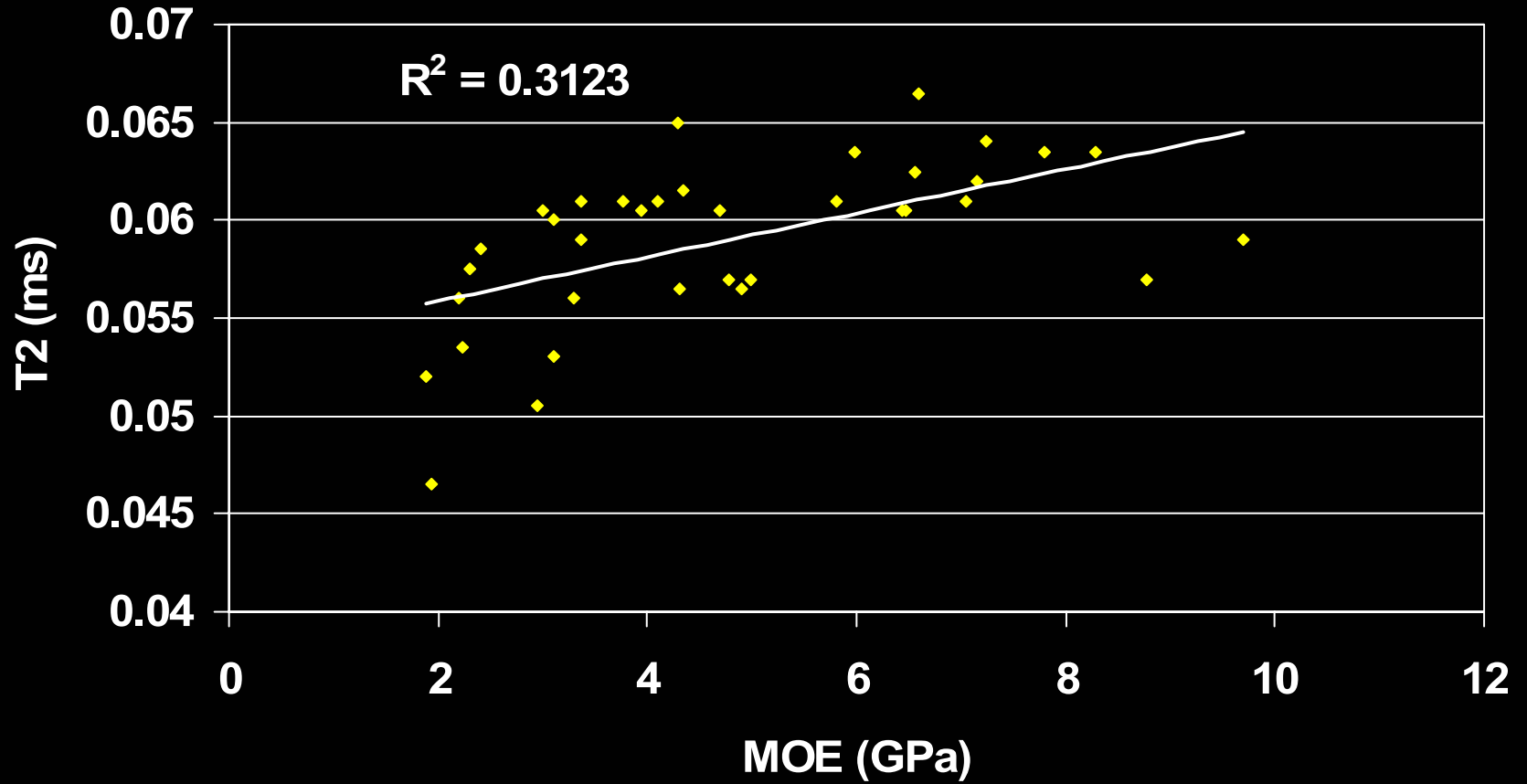


Results

Mechanical Properties/T2



Overall Correlation



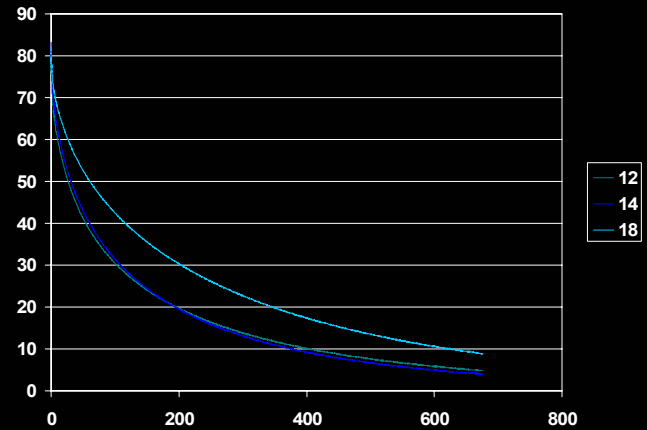
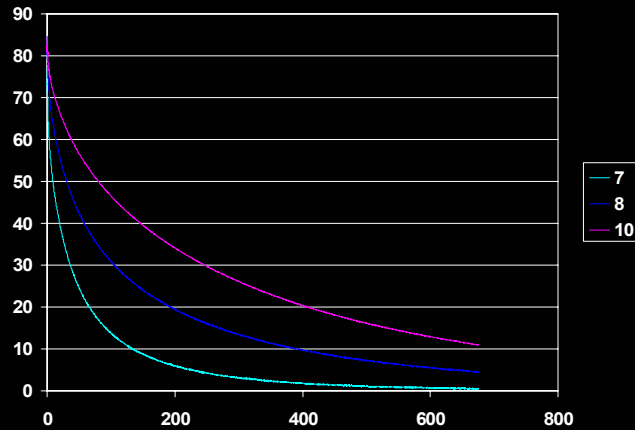
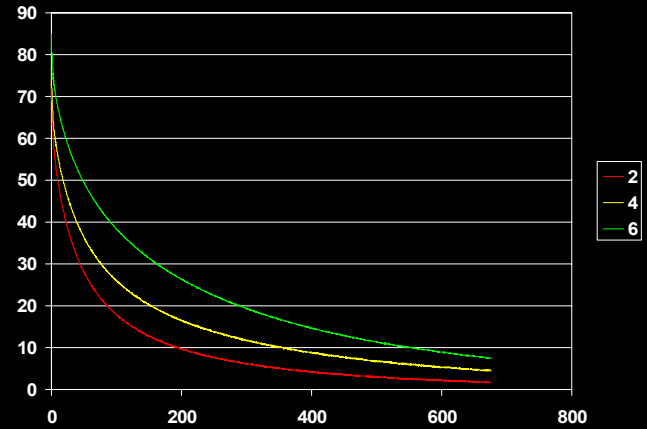
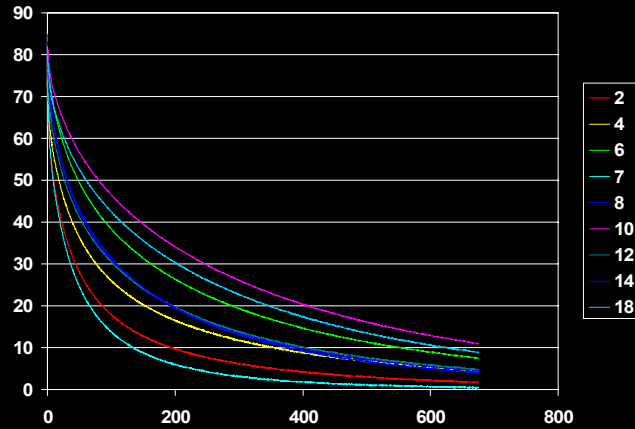
Mechanistic Questions

- For synthetic polymers T2 decreases with DP
- In the current work T2
 - generally decreases with pressure
 - increases with MOE
 - This is interpreted as “hardening” of the cell wall as a function of processing

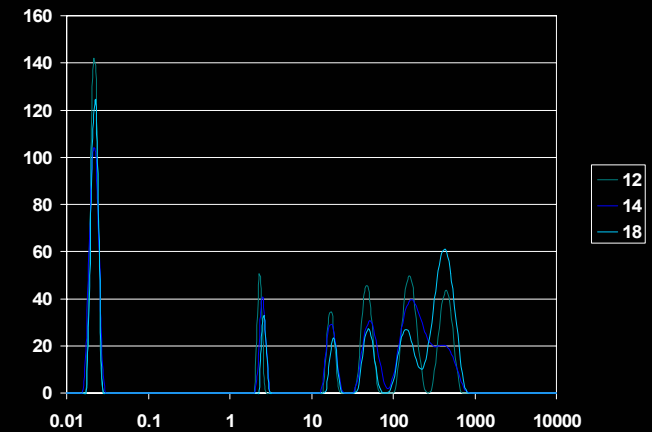
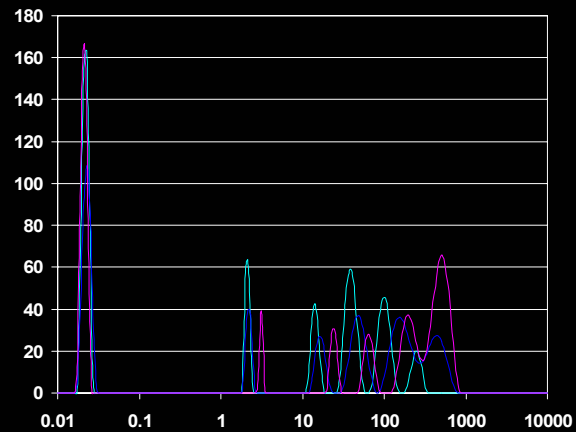
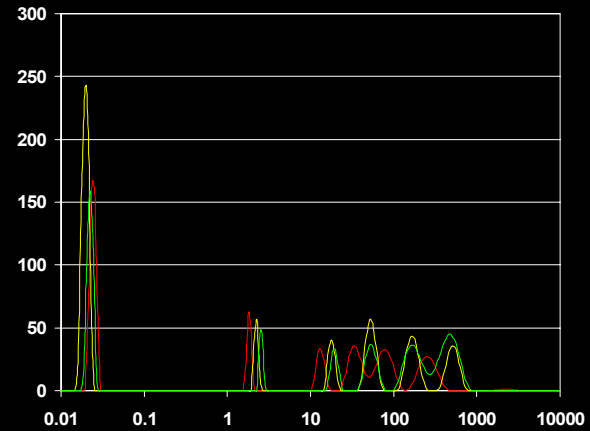
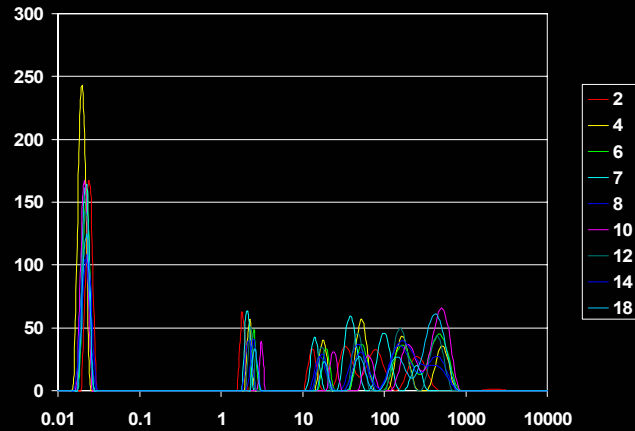
Free Water Experiments

- The MDF furnish absorbs a large amount of water, such that even with proportions of 0.25g fiber/1ml of water, there is little water apparent
- Soak fibers in a large excess of water, under vacuum for 24 hours and filter.
- This should insure that the fibers are well above FSP and the cell walls are fully saturated by bound water

Mature fibers wet FID



Mature fibers wet T2 distribution

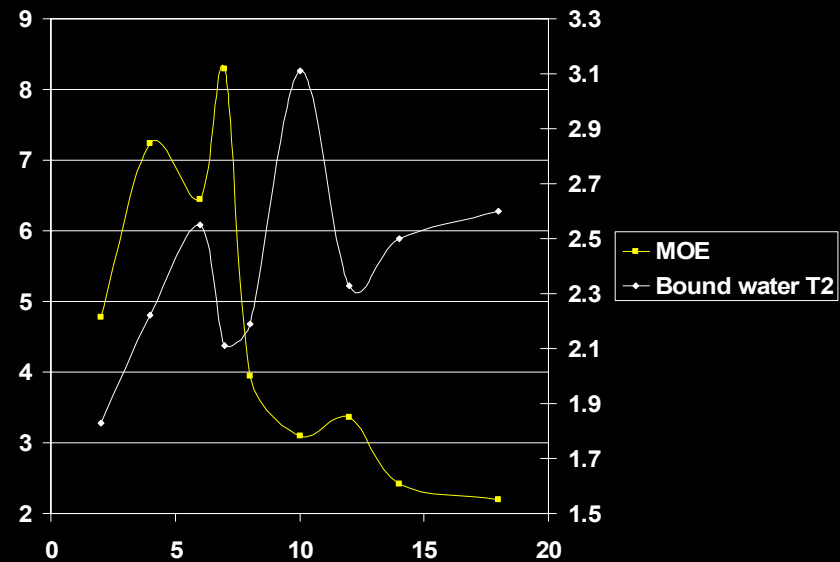


Wet Fiber Results

- These relaxation time distributions are more consistent with those reported in the literature for wood with
 - Solid matrix ~ 0.01 ms
 - Bound water ~ 1 - 2 ms
 - Free water-several peaks above ~ 20 ms

Comparison of MOE and Bound Water T2 (mature fibers)

- Both show fluctuations with pressure
- Some correspondence

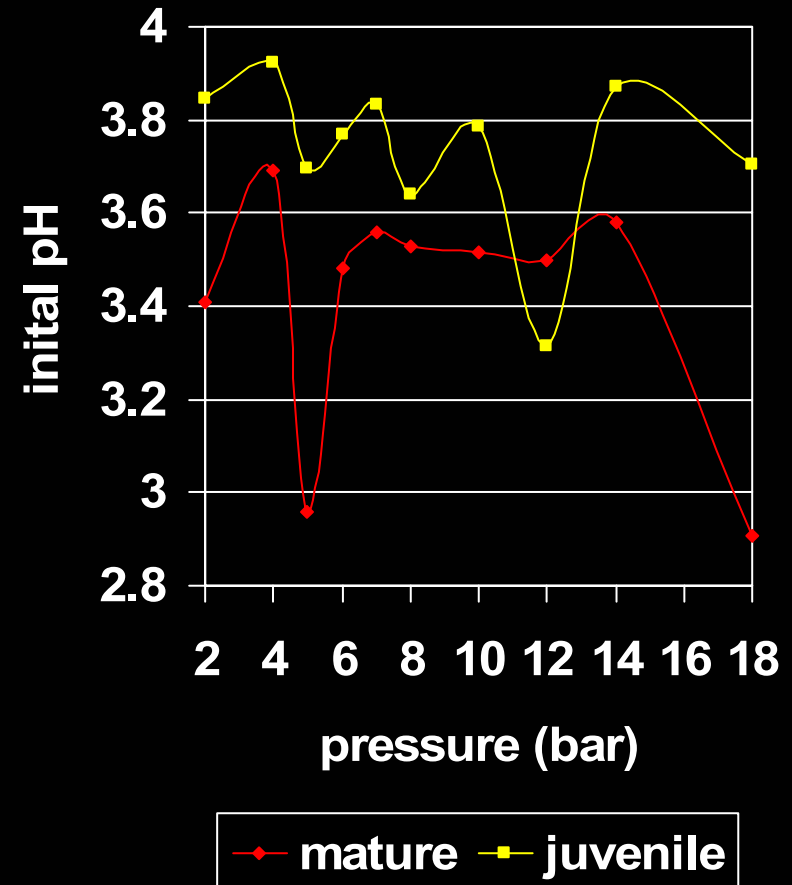


Buffer Capacity

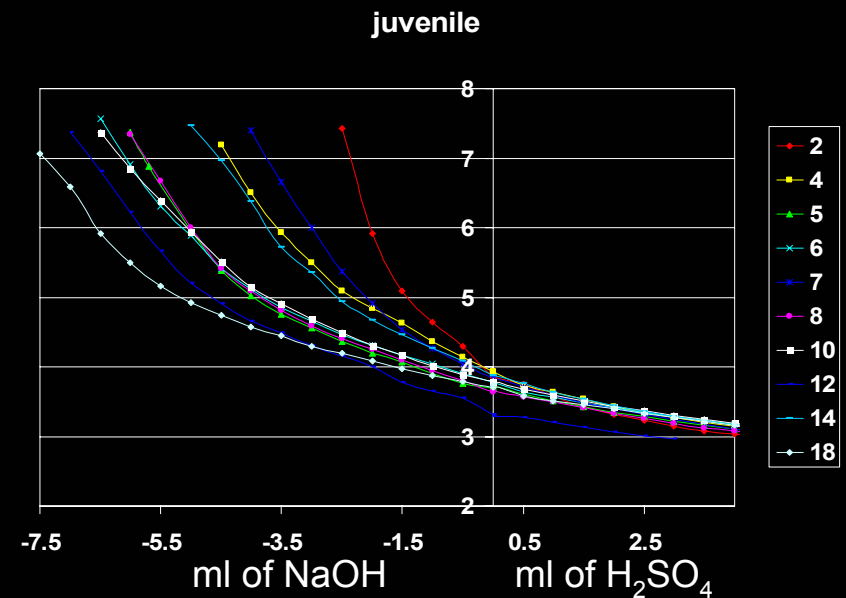
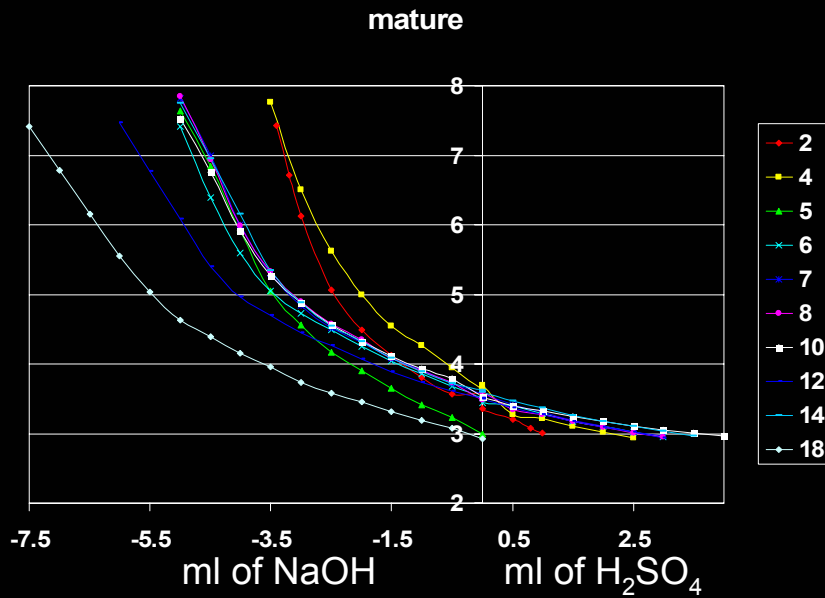
- This study was recently initiated to evaluate the acid/base characteristics of the fibers and the effect of refiner pressure
- Methods
 - Reflux fibers in deionized water for 20 minutes
 - Filter and allow the filtrate to cool
 - Measure the pH of the filtrate
 - Sequentially add 0.025N NaOH and H₂SO₄
 - After each addition, measure the pH
 - Add acid or base to lower the pH to 3 or raise it to 7.

Buffer Capacity

- To date, the mature and juvenile fibers have been assayed
- Mature fibers
 - The initial pH is acidic, with two points (5 and 18) below 3.
 - There is a plateau from pH 6 to 14
- Juvenile fibers
 - Less acidic
 - More variable

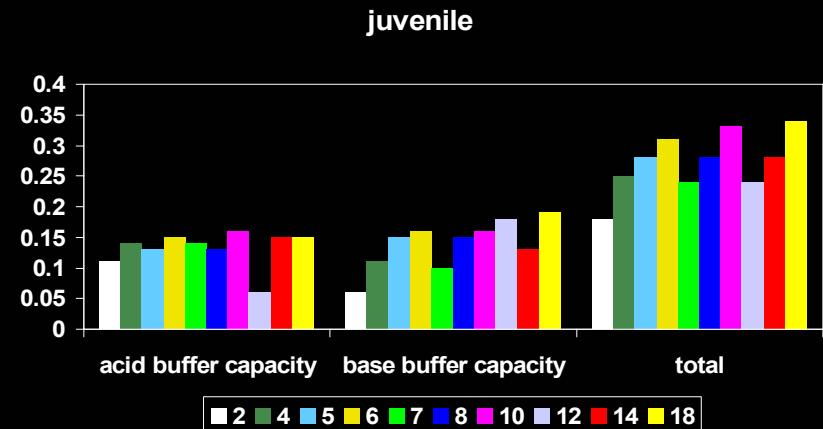
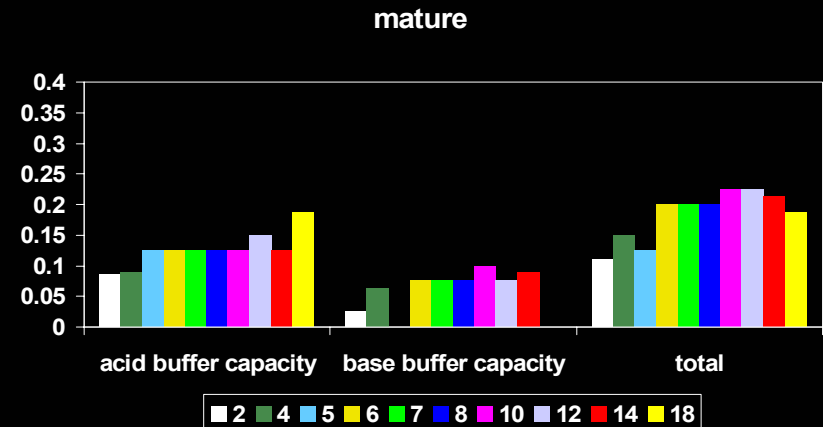


Buffer Capacity Curves



Buffer Capacity

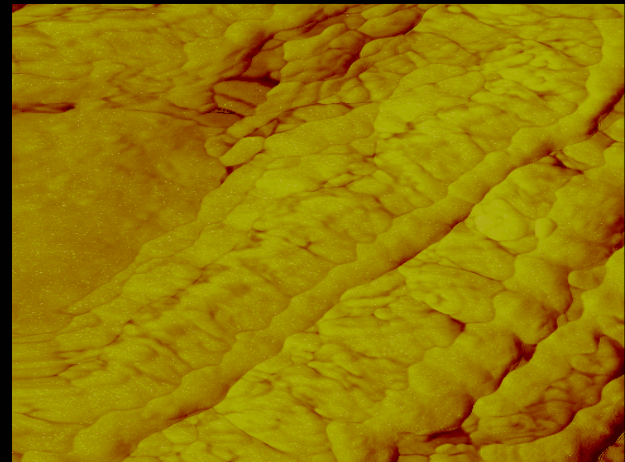
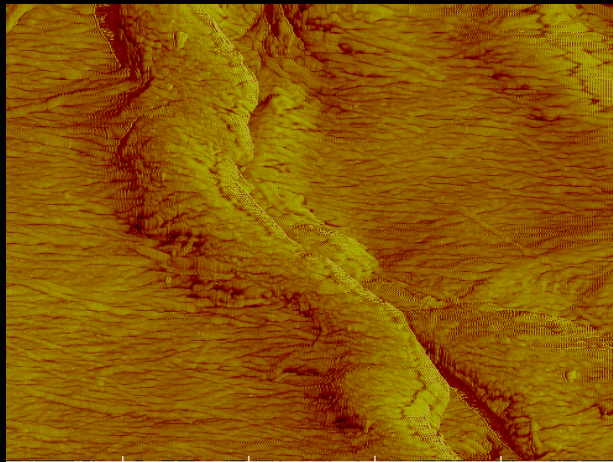
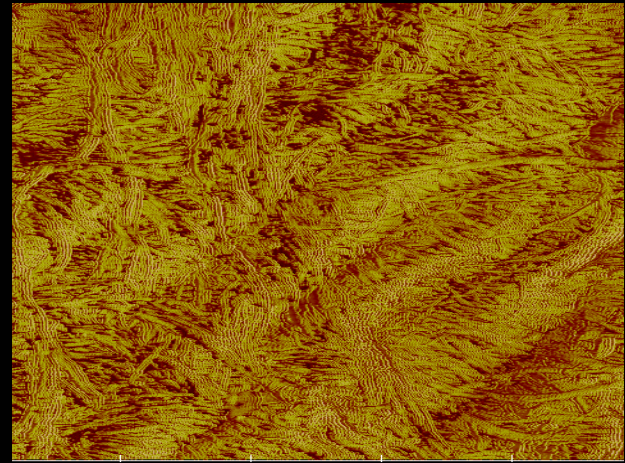
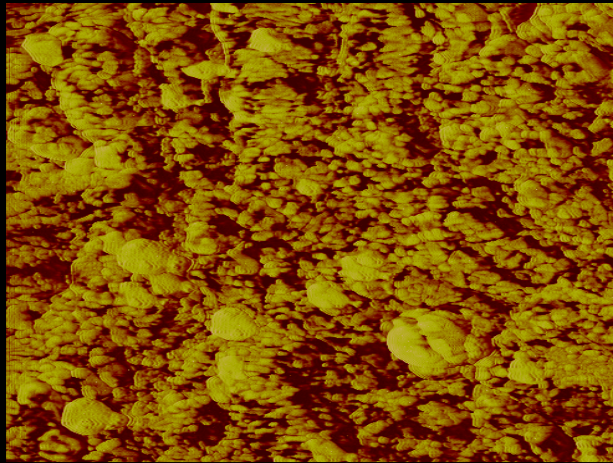
- Mature fibers exhibited a general increase in both acid and base buffer capacity with refining pressure
- The total value for the mature fibers reaches a maximum in the 10-12 bar range
- Juvenile fibers are variable with a much higher base buffer capacity, resulting in a higher total.



Effect of corona discharge on surface properties of handsheets

- TMP and bleached kraft pulps from Art Raguaskas at Georgia Tech
- Dielectric-barrier discharge
 - 0, 0.12, 3.31 and 9.27 kW/m²/min
 - AFM
 - IGC

Effect of corona discharge on surface properties of bleached kraft pulp



AFM on TMP

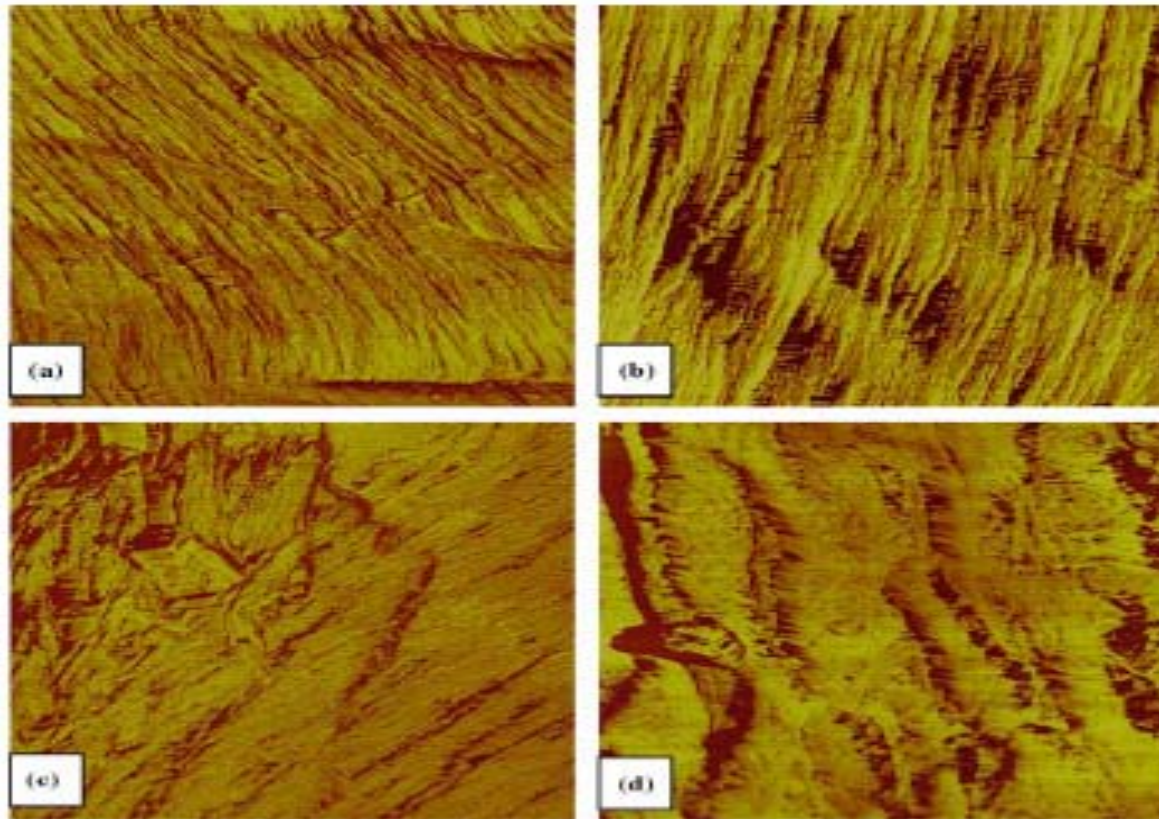
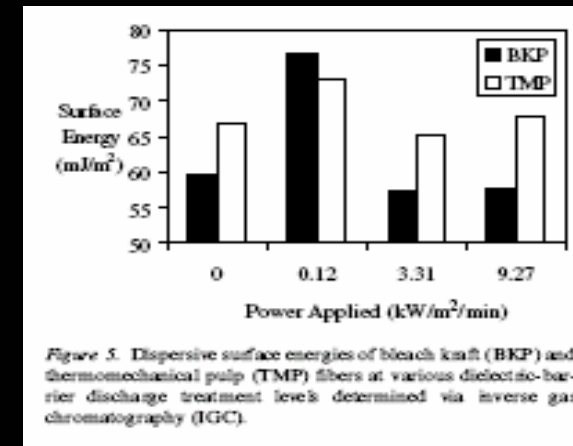
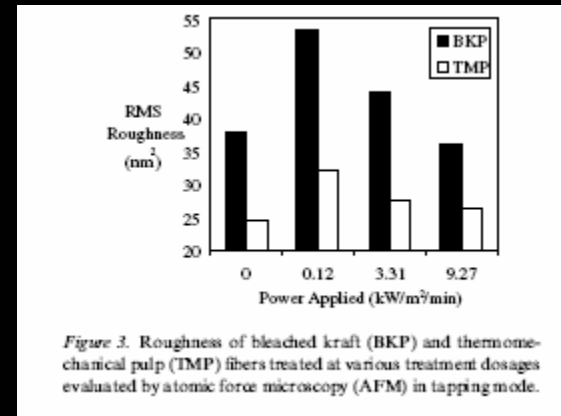


Figure 2. Atomic force microscopy (AFM) phase images of thermomechanical pulp fibers treated at 0 kW/m²/min (a), 0.12 kW/m²/min (b), 3.31 kW/m²/min (c), and 9.27 kW/m²/min (d) dielectric-barrier discharge treatment levels.

Roughness data for pulp samples

- Roughness results corresponded well to mechanical properties of the pulp and the surface energies from IGC
- These results, indicating a large change at the low treatment level are consistent with the mechanical properties of the fibers.



Thermal Degrade of Wood Fiber Study

Infrared and NMR Analyses
Collaboration with Jerry Winandy
at USDA-FS-FPL

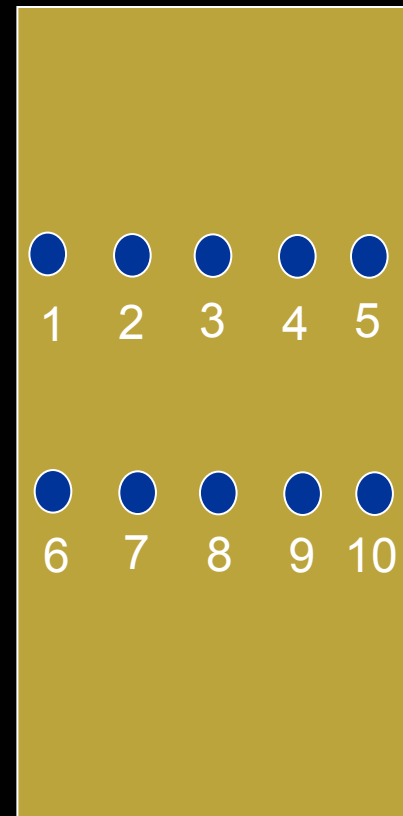
Methods

- Samples of medium density fiberboard furnish were pressed into panels at the indicated conditions of temperature and time.
- For enhancement of dimensional stability and decay resistance

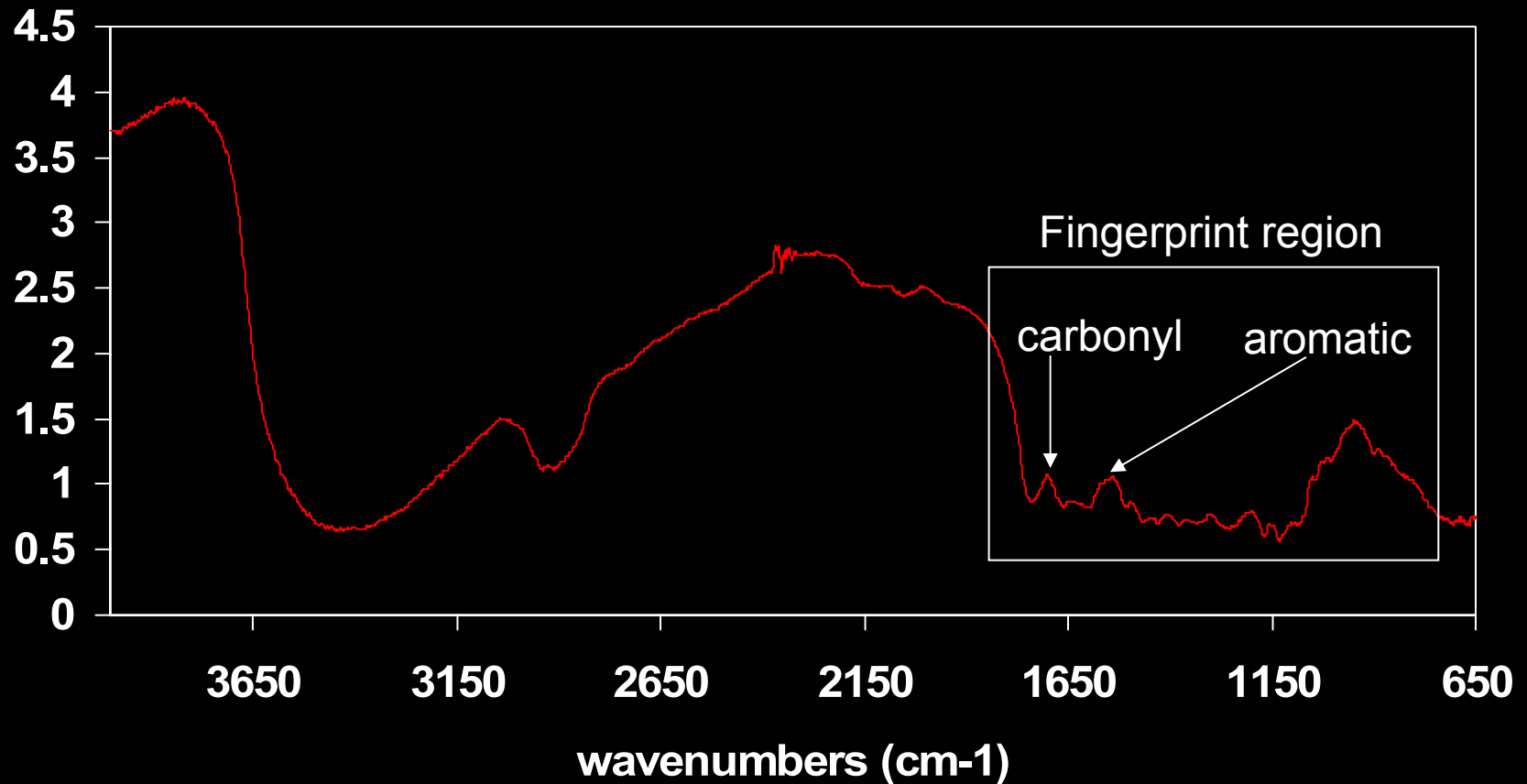
Panel code	Temp (C°)	Time (secs)
a-1	180	180
b-1	180	270
c-1	180	360
d-1	180	450
e-1	180	540
e-2	180	720
e-3	180	900
e-4	180	1080
f-1	200	180
g-1	200	270
h-1	200	360
k-1	200	450
l-1	200	540
m-1	200	630
n-1	200	720
p-1	200	810

Methods

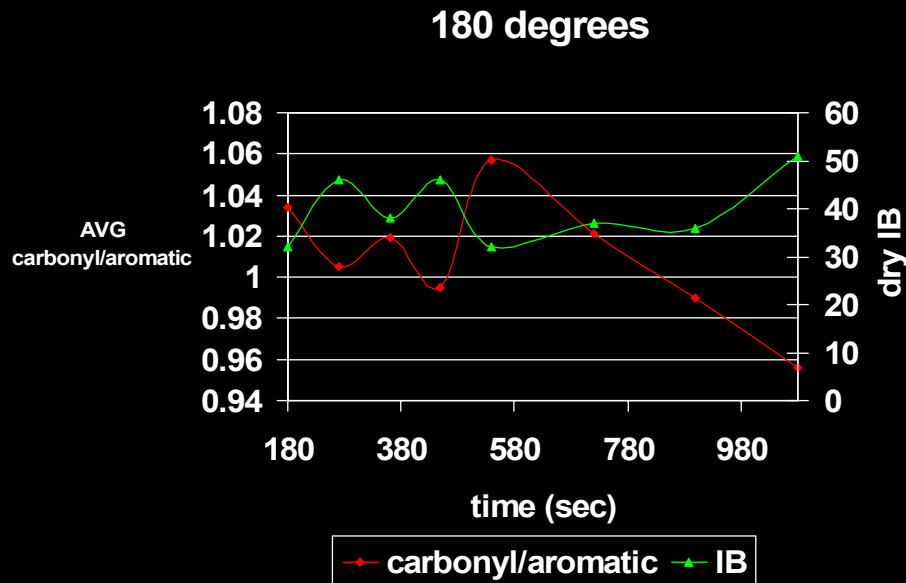
- Samples of each panel were cut across the thickness
- Infrared spectra were collected using a Nicolet-Nexus 670 FTIR, with a Continuum Microscope
- Spectra were taken from areas 150μ square, in reflectance mode, at the positions indicated.



Typical reflectance spectrum



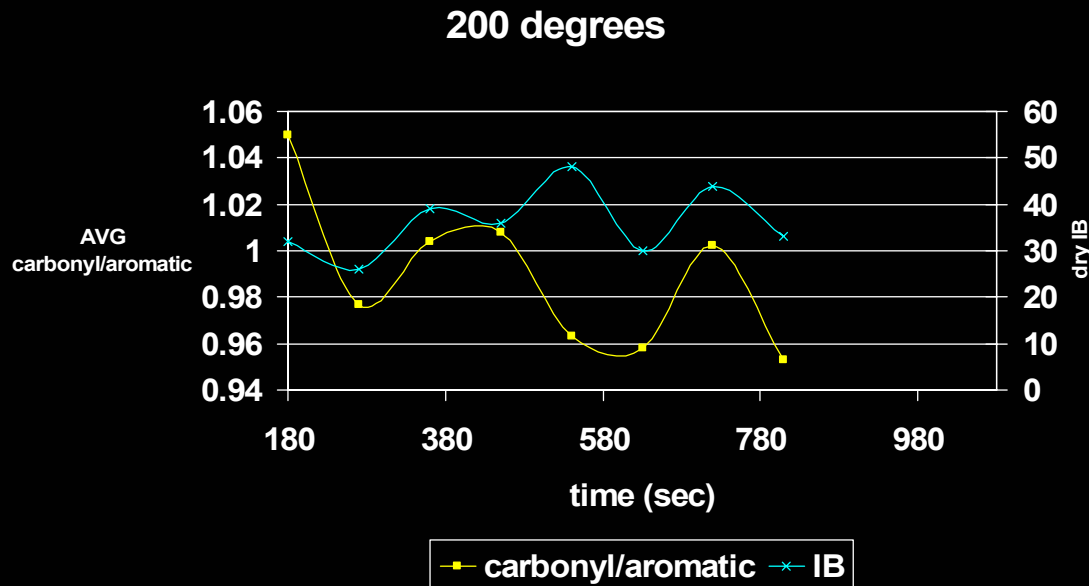
AVG carbonyl/aromatic



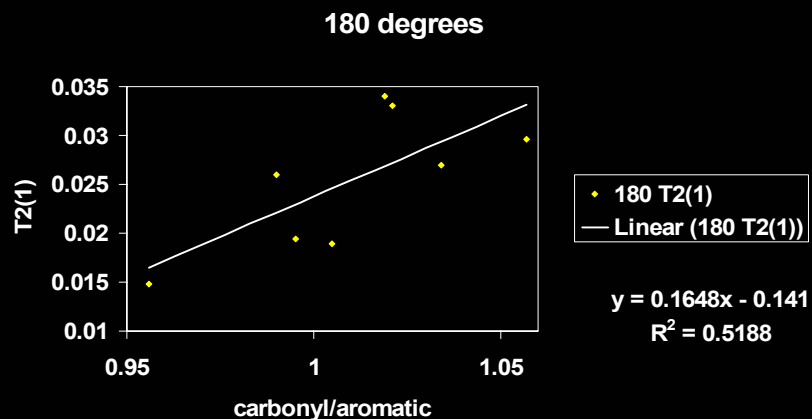
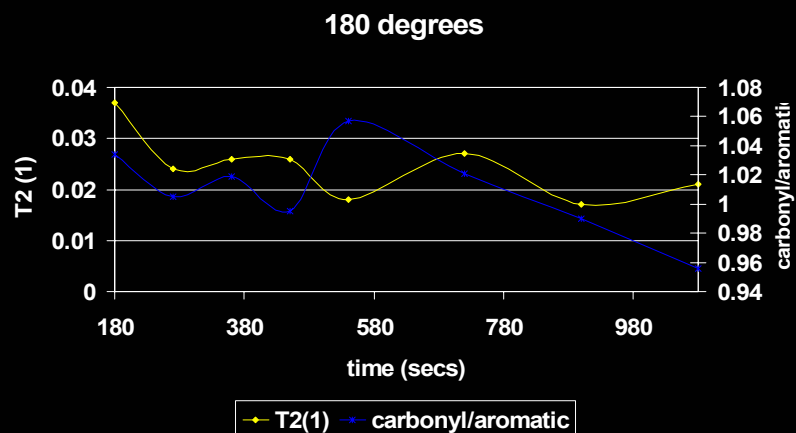
- The carbonyl/aromatic ratio is a measure of oxidation
- At the short times at 180°, this appears to be an inverse relationship with IB

AVG carbonyl/aromatic

- At 200°C the carbonyl/aromatic ratio seems to be somewhat more positively related



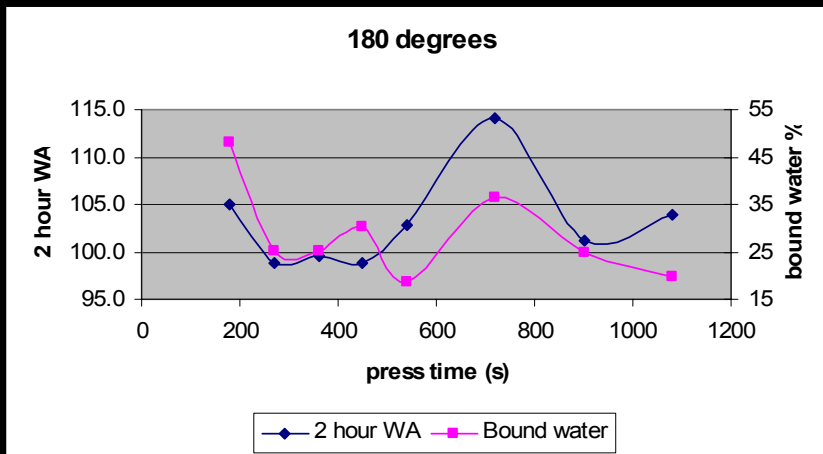
T2 relaxation time vs oxidation



- A plot of the short relaxation time, representing the solid matrix vs the carbonyl/aromatic ratio is similar.
- This linear relationship suggests that NMR can be used as a reaction index.

Water absorption and bound water

- The amount of bound water present, as determined by NMR closely parallels the water absorption.



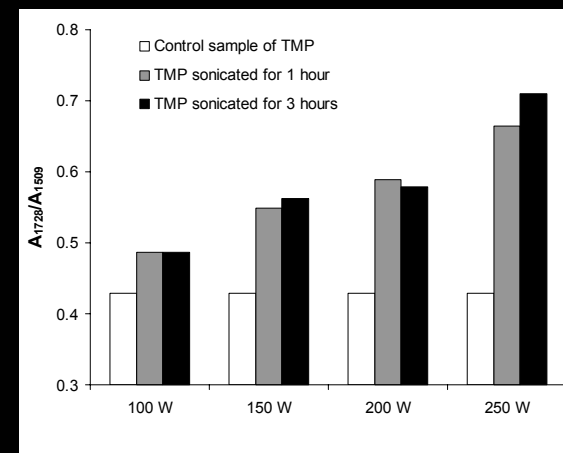
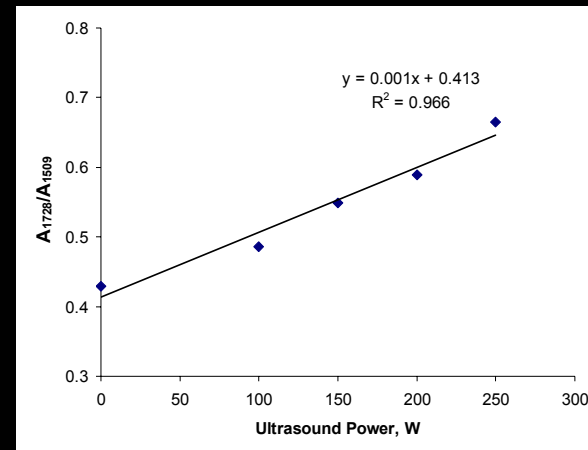
High Frequency Ultrasound in Fiber Modification

Collaboration with Jayant Gadhe and Ram Gupta, Department of Chemical Engineering, Auburn University

- When an aqueous suspension is treated with ultrasound, cavitation is induced in the liquid, decomposing water into free radicals.
 - $\text{H}_2\text{O} \rightarrow \cdot\text{H} + \cdot\text{OH}$
- Low frequency ultrasound (~25kHz) has been used and reported
- High frequency (610kHz) was used in this work
 - High frequency gives shorter bubble lifetimes and more free radicals
 - High frequency is quieter

High Frequency Ultrasound in Fiber Modification

- Constant frequency (610mHz)
- Variable power (control, 100, 150, 200, 250W), 1 and 3 hours
- FTIR results (A_{1728}/A_{1509}) on MDF furnish
 - Linear increase in oxidation with power and time



Summary

- Changes in process (refining pressure) results in chemical and physical changes
 - Both mechanical properties and NMR results vary with pressure
- Plasma treatments at low energy levels result in largest property differences (which are consistent between assays)
- NMR, FTIR, IB and water absorption vary with time and temperature of heat treatments
- Ultrasonic treatment results in linear increase in oxidation as a function of time and power