Low-Field, Time-Domain NMR and its Application to Wood Science and Technology

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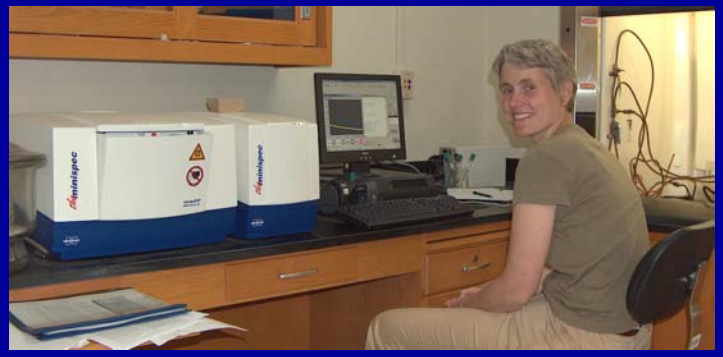

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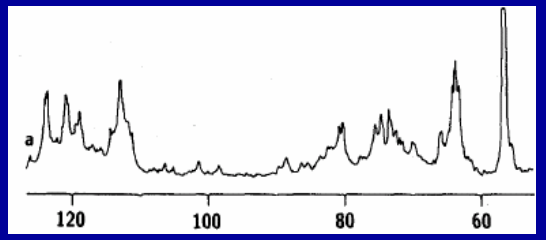
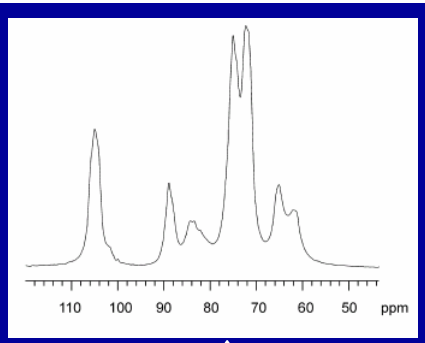
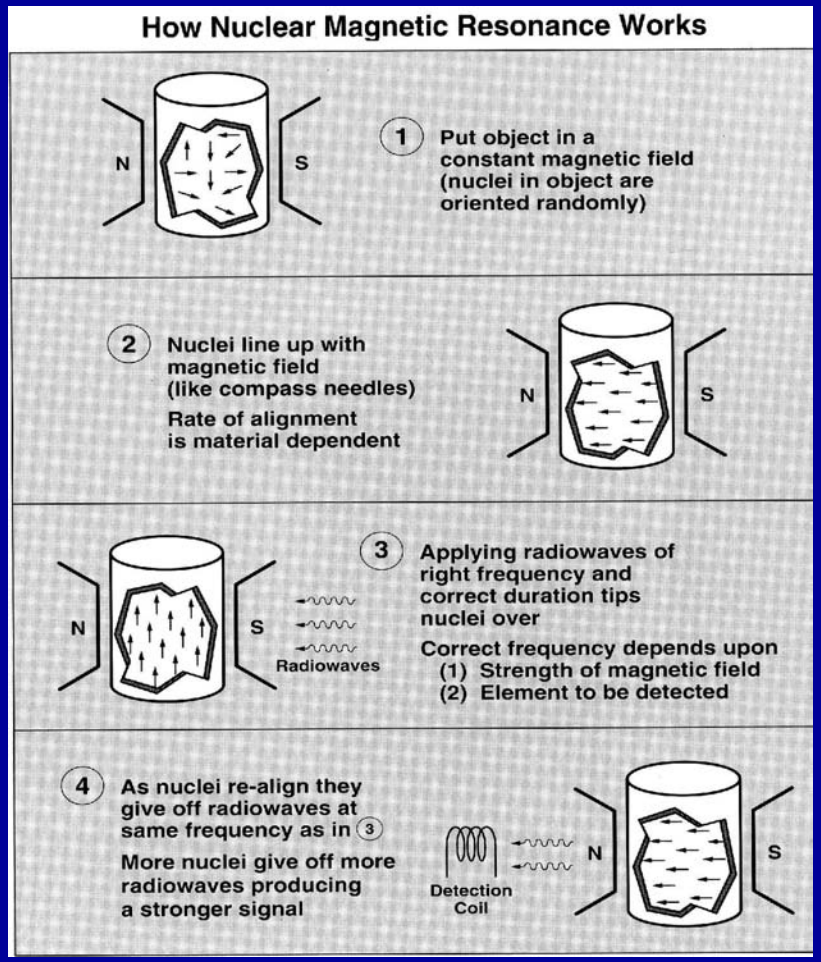
NMR

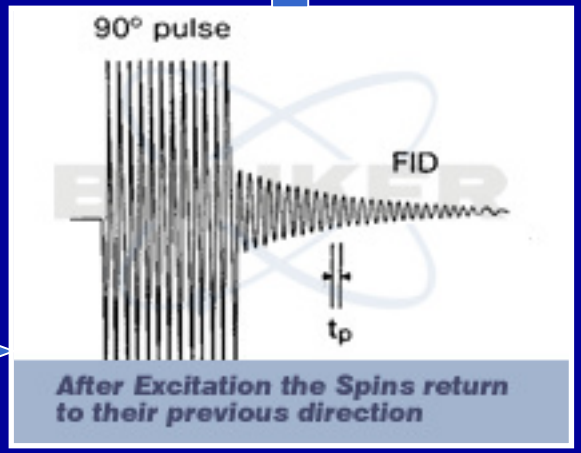
Frequency domain





Fourier transform





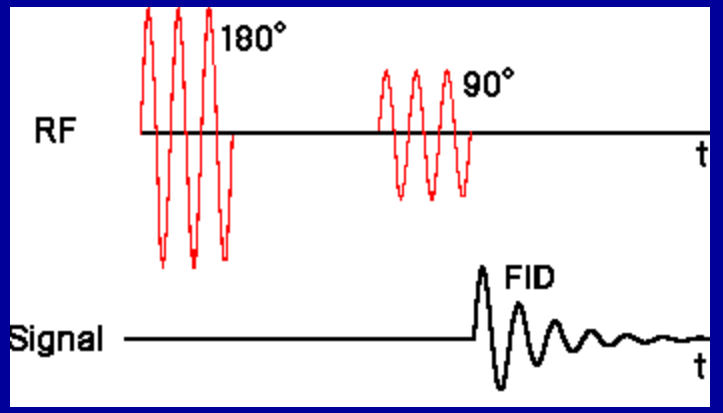
Time domain

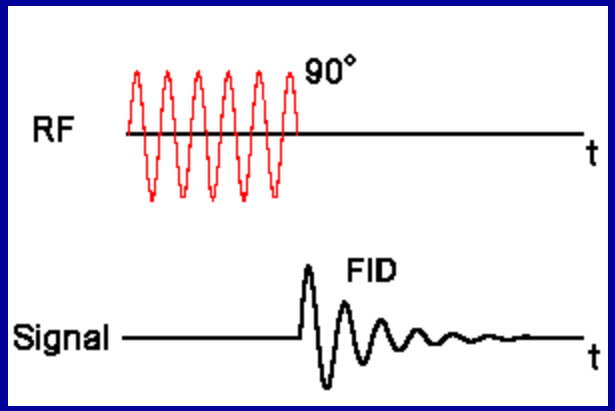
Time Domain NMR

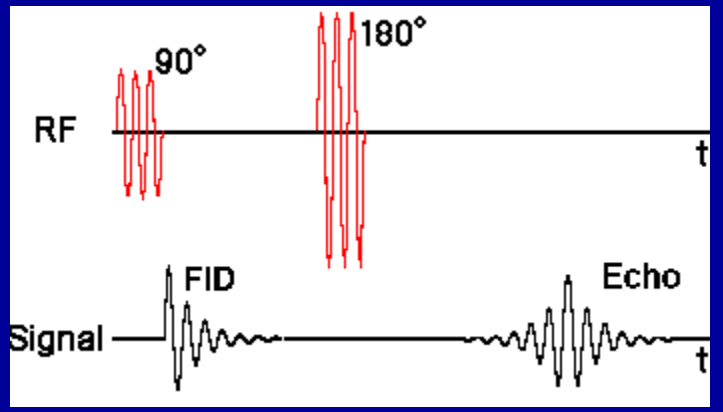
- The time required for the nuclei to return to equilibrium after excitation is the “relaxation time” (this type of NMR is sometimes referred to as “relaxometry”)
- T1 relaxation or spin-lattice or longitudinal relaxation.
  - Energy is dissipated to the molecular framework
- T2 relaxation or spin-spin or transverse relaxation.
  - Energy is dissipated to neighboring nuclei.
- Nuclei in different environments have different T1 and T2 relaxation times

NMR Experiments

- For T1 determination:
  - Inversion recovery
- For T2 determination:
  - Free Induction Decay
  - Hahn Spin-Echo sequence
  - CPMG

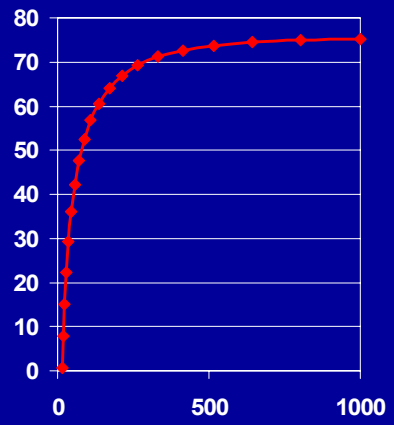


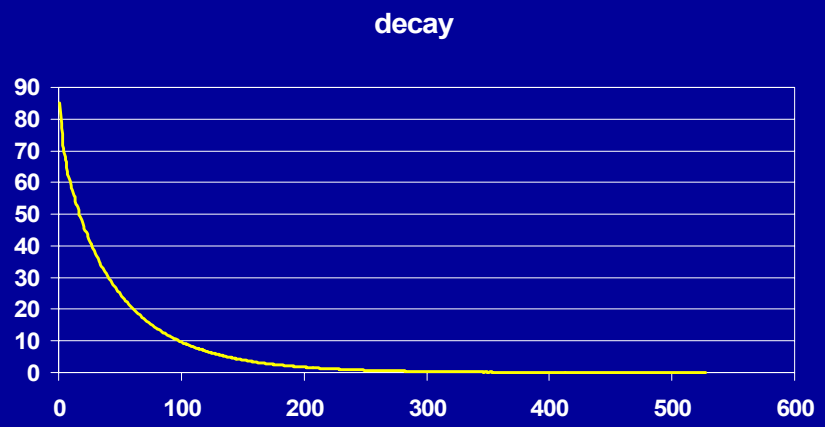




Fitting Decay Curves

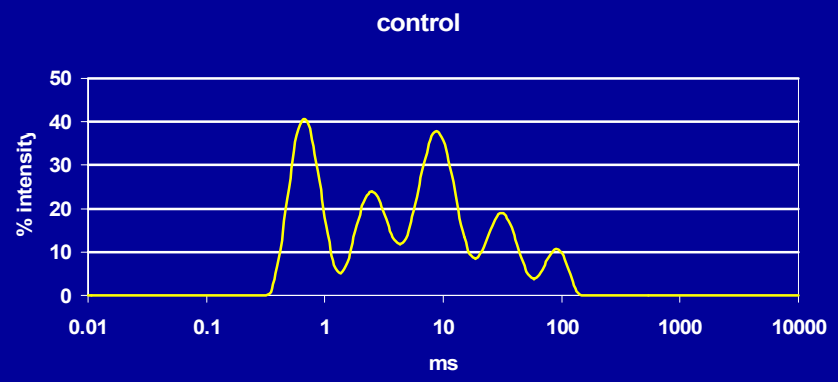
- The simplest way to determine T2 is as 36.8% of maximum signal
- Fit exponential functions
- Mixtures of gaussian and exponential functions
- These generally give discreet values for relaxation times
- FID of solids are not fit by exponentials
- Liquids can be fit by exponential functions





Relaxation Time Distributions

- These methods can fit multiexponential functions
- Width and position provides information about the various environments
- Methods
  - Contin
  - UPEN
  - NNLS
  - MVA



Applications of Time Domain NMR

- MRI
- Geology
  - porosity
- Food
  - Water/fat content
- Textiles
  - Fabric finishes
- Cosmetics
- Polymers

Low-Field NMR

- Typical analytical spectrometers operate at several hundred MHz
  - FT converts the time domain information to the frequency domain
- The same thing can be done with a low field (20-60 MHz) instrument but the spectrum is poorly resolved
- Alternatively, information can be extracted on relaxation times (the time required for the atoms to return to equilibrium after the RF pulse)

Low-field NMR spectrometers (not exhaustive or inclusive)

- Bruker Optics (minispec)
- Oxford Instruments (Maran)
- Magritek
- Tel-Atomic
- Process NMR
- One sided NMR
  - NMR-Mouse
  - Minispec Profiler

one-sided NMR

Advantages and Disadvantages of Low-Field NMR

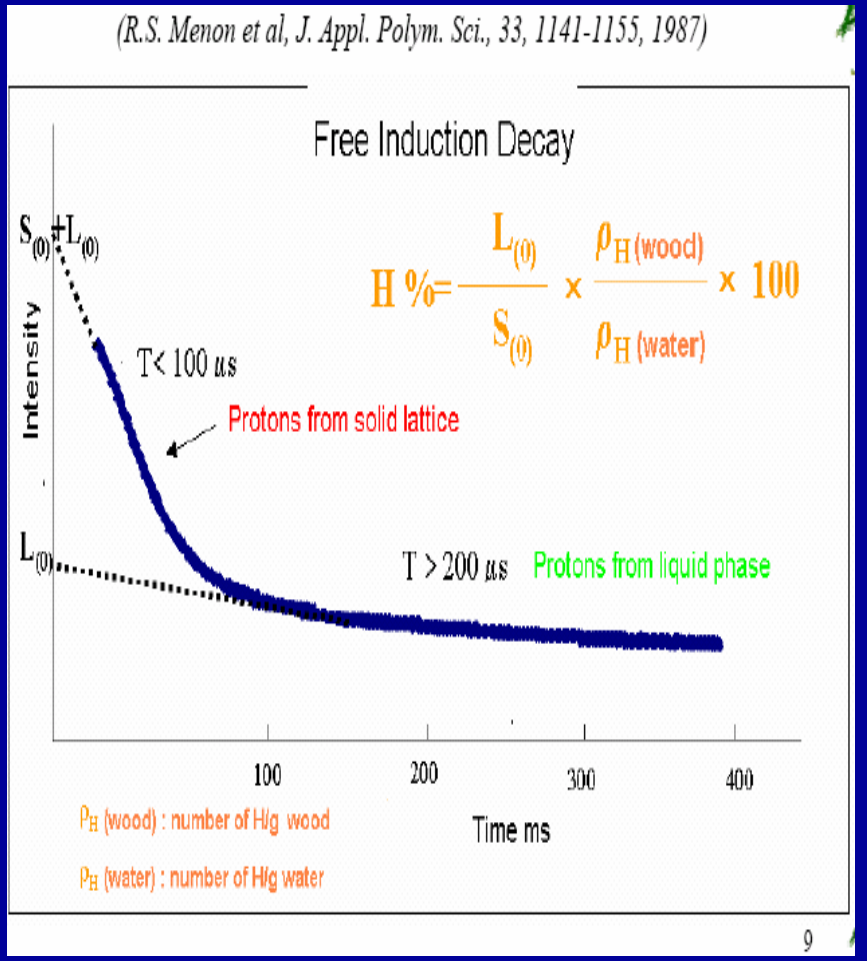
- No frequency domain spectra
- Accept both solids and liquids
- Limited sample preparation
- Large sample sizes
- Long dead time (9-38 μs)
- Detects hydrogen, phosphorus, fluorine
- Little maintenance
- Ease of operation
- Relatively inexpensive

Examples of Literature on Time-Domain NMR of Wood

- Moisture interactions and Imaging
  - UBC/Forintek (MacKay, Hartley, Araujo, Menon)
  - Labbé
  - Ye (OSB)
- Porosity and Diffusion
  - STFI (Häggkvist et al.)
  - Lund University (Topgaard and Söderman)
- Paper
  - Capitani et al.
- Fungi
  - Gilardi
  - Müller
- Black Liquor
  - Draheim and Ragauskas
- Adhesives
  - Pizzi
  - Root and Soriano
- Cell and Ring size
  - Wycoff
  - Johannesen
- Thermal
  - Hietala et al.
- pH
  - Ahvazi and Argyropoulos
- Wood-Adhesive interactions
  - Frazier

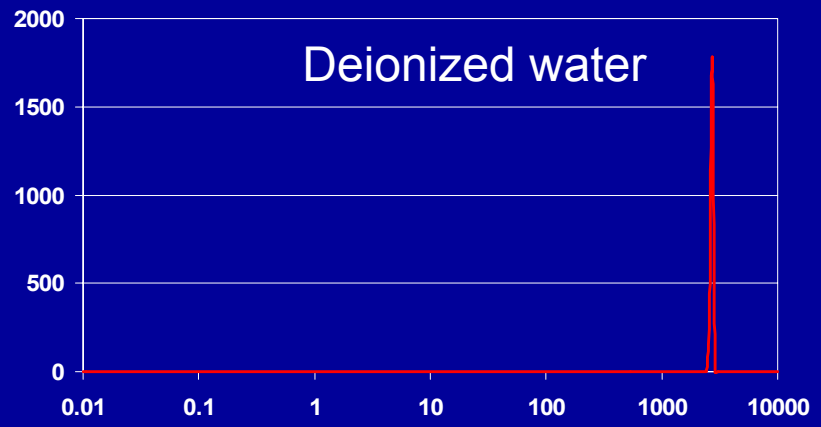
Relaxation Times for Wood Components

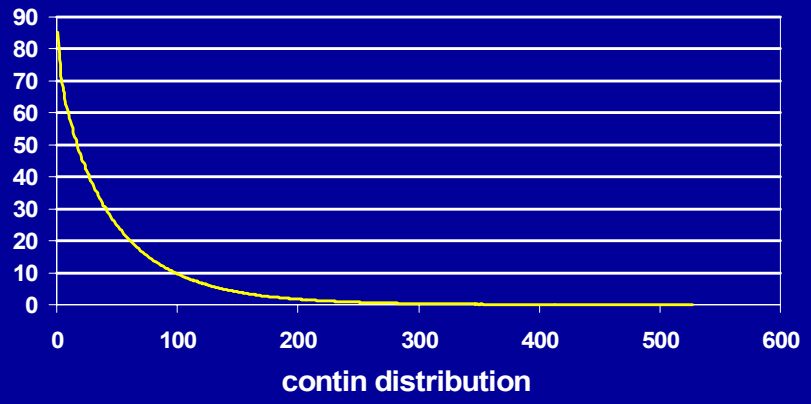
- Solid matrix
  - Fastest relaxation times T2<1 ms (Labbé et al. 2002)
- Bound water
  - T2 ~ 1ms
- Free water
  - T2 ~10-100 ms
- Extractives
  - T2 ~7-150 ms (Labbé et al. 2002)
- Detecting the hydrogens in the solid matrix requires a short dead time
- FIDs of solids are not fit well by exponential functions so it's difficult to extract accurate relaxation times

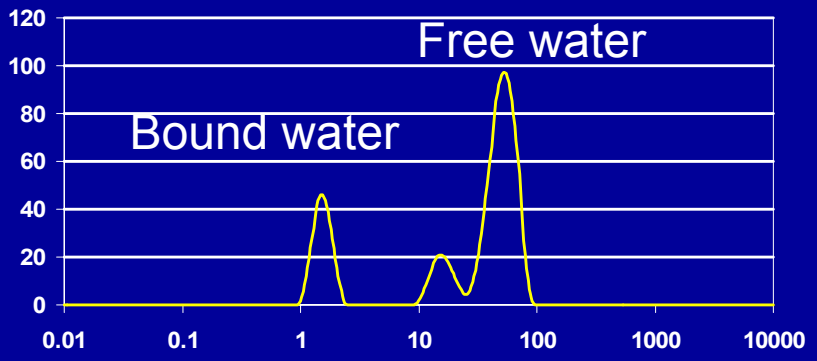


Relaxation Times for Wood Components

- Liquids are well described by exponential functions
- As such, water in various environments in the woody cell wall can be detected and analyzed
- This has mainly been done by the analysis of T2 by CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence.







Current work on Low-field 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) (CPMG experiments)
- Decay curves were analyzed using Contin to determine distributions of relaxation times

Furfuryl Alcohol Modified Wood

- Introduction
  - Modification with furfuryl alcohol is proposed as a method for improving dimensional stability of wood and its resistance to biological degradation.

Furfuryl Alcohol Modified Wood

- Polymerization
  - Furfuryl alcohol in the presence of a catalyst forms Poly(FA)
  - The polymer and the mechanism by which it is formed is complex
    - Head-to-tail and head-to-head dimers are initially formed
    - Conjugated chromophore segments are also produced.

Methods

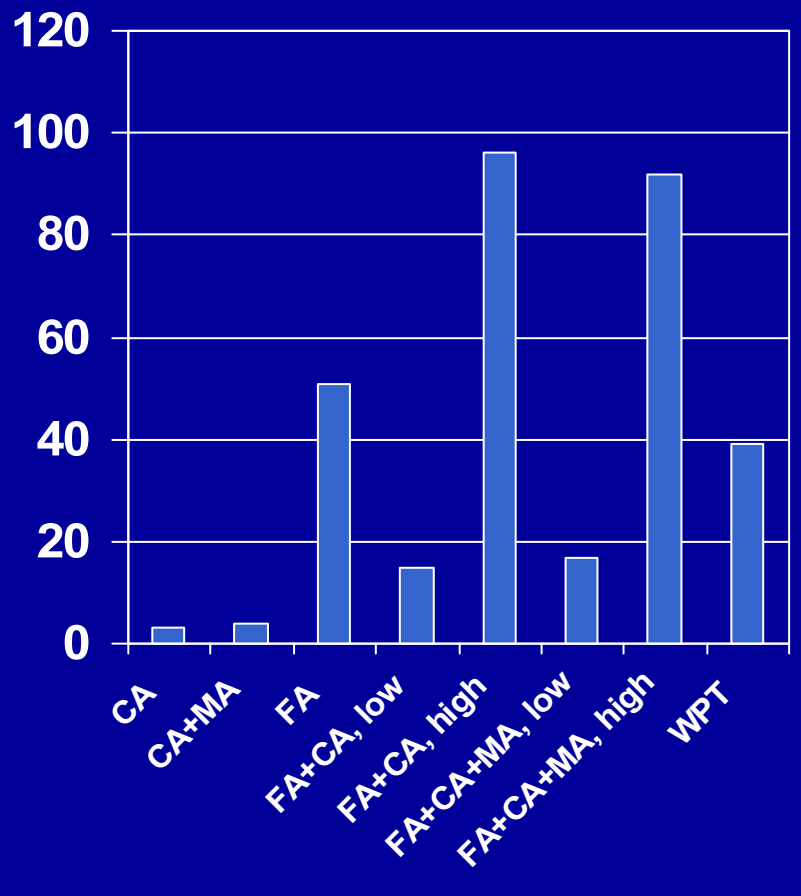
- Scots pine (*Pinus sylvestris*) was collected from northern Zealand in Denmark
- Samples were machined to 15x25x30 mm and conditioned at 20°C at 65% RH
- Samples were treated by
  - Pre-drying-at 103°C for 16 hours
  - Impregnation-under vacuum
  - Curing-wrapped in aluminum foil and cured at 103°C for 16 hours
  - Drying-40°C for 144 hours

Methods

- Sample treatments
  - Furfuryl alcohol (FA)
    - Undiluted (98%)
  - Citric acid (CA)
    - 2% in DI
  - Citric acid (CA)+maleic anhydride
    - CA (2%)+MA (1%) in DI
  - FA+CA, low WPG
    - FA(20%)+CA (0.77%)+ETOH(77%)+DI(2.23%)
  - FA+CA, high WPG
    - FA(72.5%)+CA(2.78%)+ETOH(19.7%)+DI(5.02%
  - FA+CA+MA, low WPG
    - FA(22.6%)+CA(0.25%)+MA(0.125%)+DI(5%)
  - FA+CA+MA, high WPG
    - FA(72%)+CA(1%)+MA(0.5%)+ETOH(19%)+DI(17.5%)
  - WPT
    - Commercial furfuryl alcohol treatment

Results

- Weight gain
  - CA, 3%
  - CA+MA, 4%
  - FA, 51%
  - FA+CA, low, 15%
  - FA+CA, high, 96%
  - FA+CA+MA, low, 17%
  - FA+CA+MA, high, 92%
  - WPT, 39%

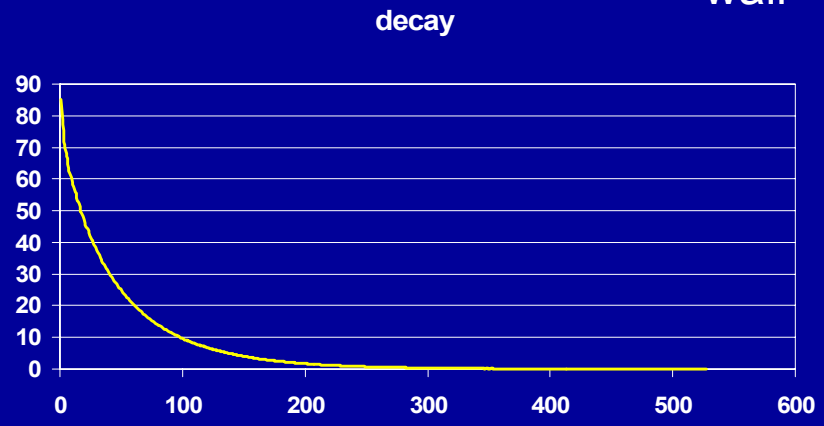


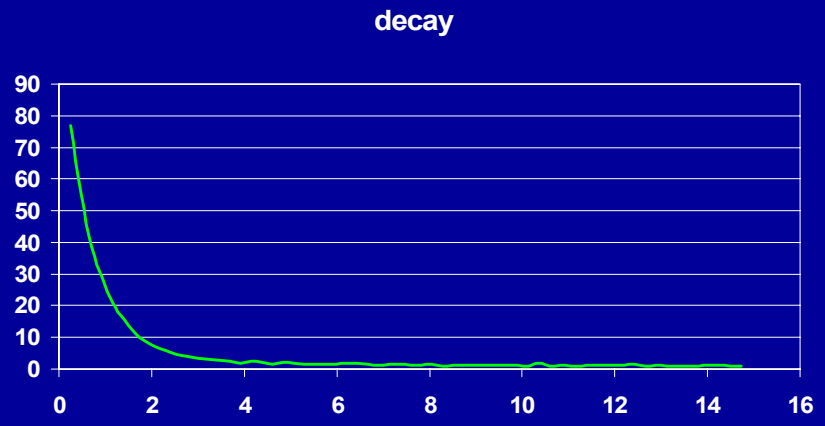
Low-field Time-domain-NMR

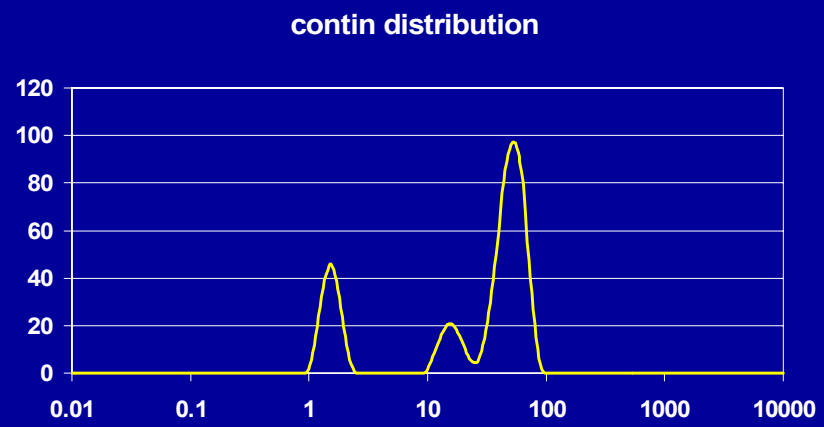
- Samples were placed into 18mm diameter test tubes, covered with water, a vacuum was applied, and the samples were conditioned for a week.
- NMR parameters
  - CPMG experiment
  - Tau=0.5ms
  - 512 echoes
  - 32 scans
  - 5 second recycle delay
  - Gain was tuned for each sample
- Decay curves were analyzed using Contin to determine distributions of relaxation times

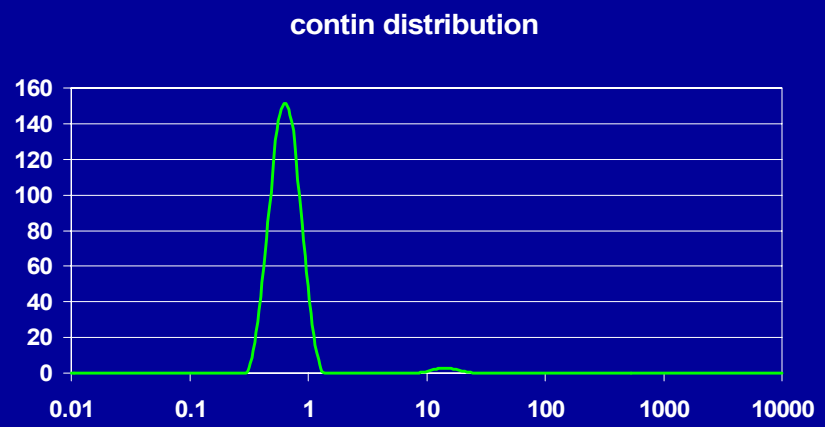
Control

- Decay curves are exponential
- T2 results show peaks for bound water, ~1ms
- Free water appears as two fairly well-resolved peaks at about 15 ms and 50ms
- Bound water at FSP relaxes more rapidly because there is only interaction with the cell wall



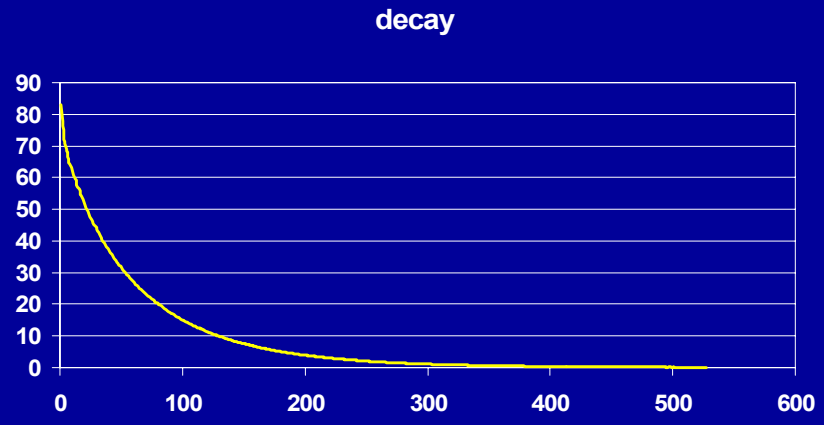


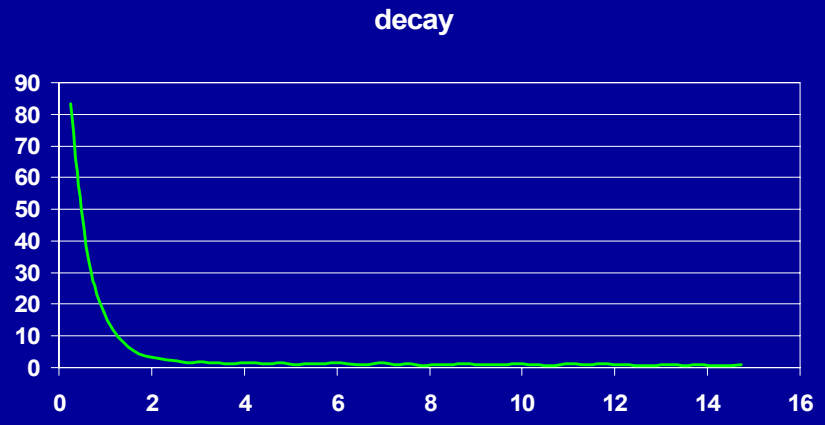


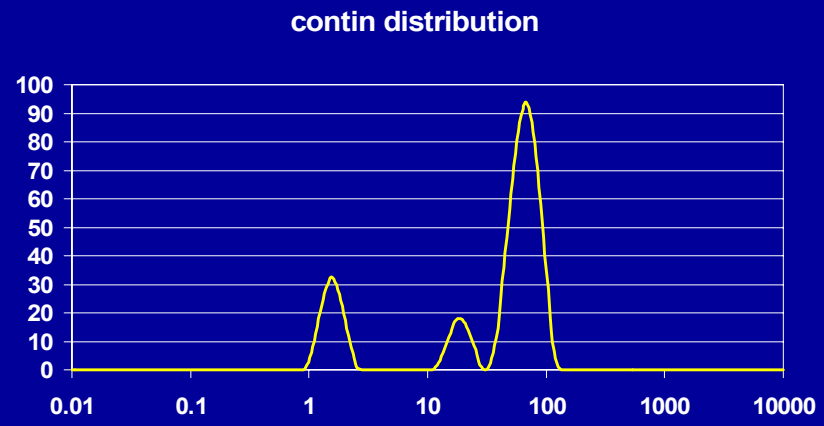


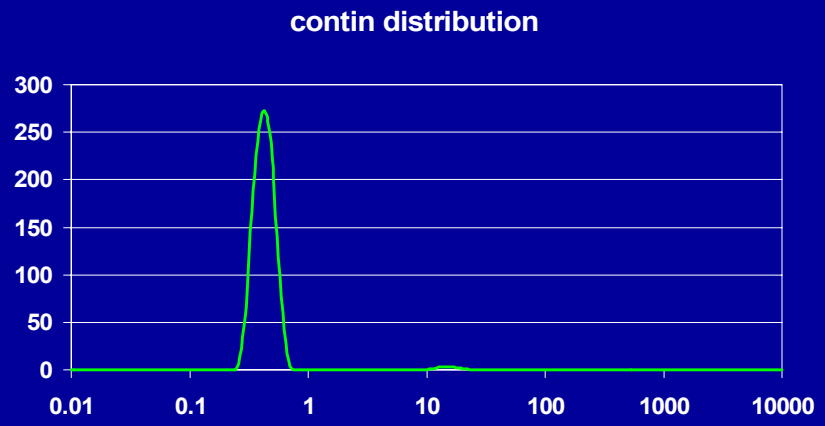
Citric Acid

- Both the decay and Contin distributions are similar to the control
  - Bound water and free water are readily evident



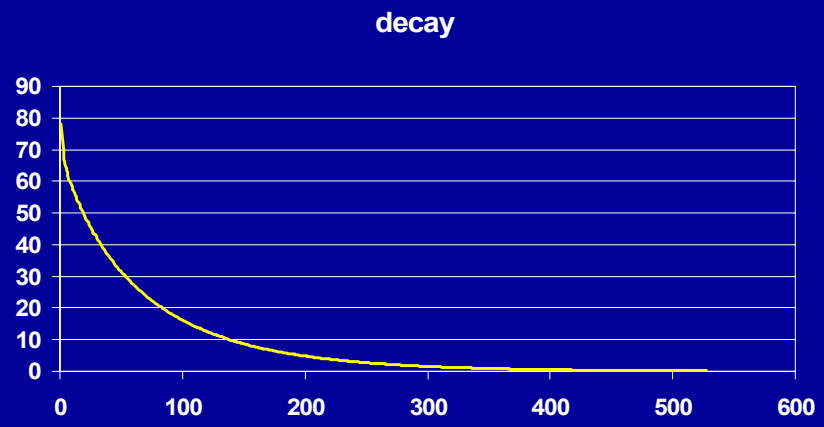


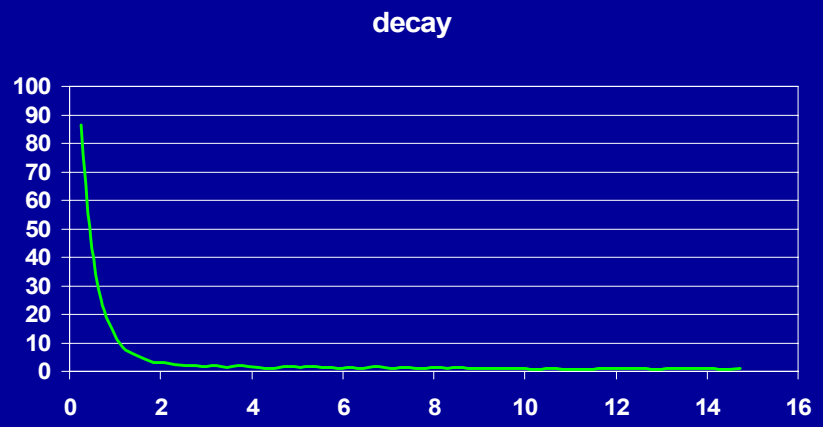


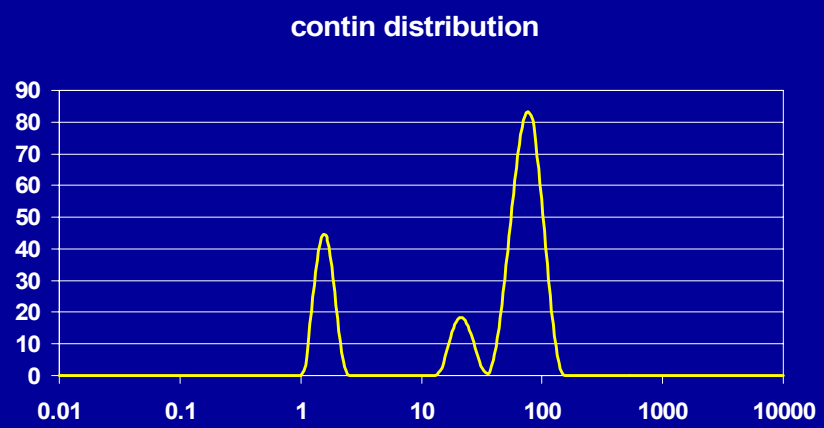


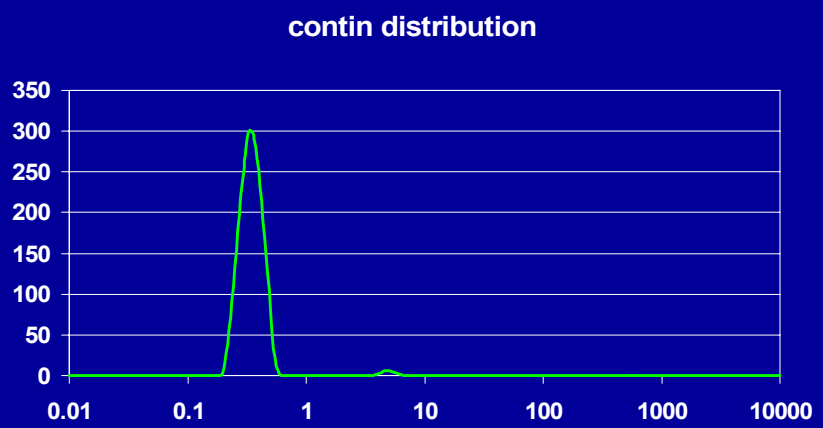
Citric acid+ maleic anhydride

- Also similar to control

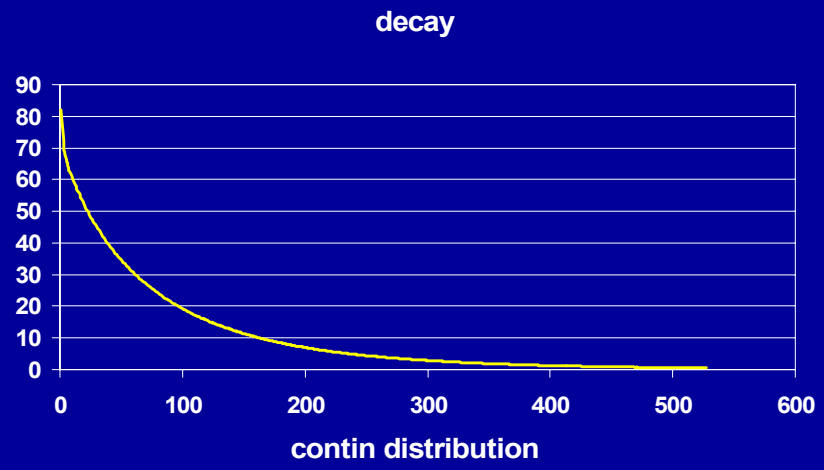


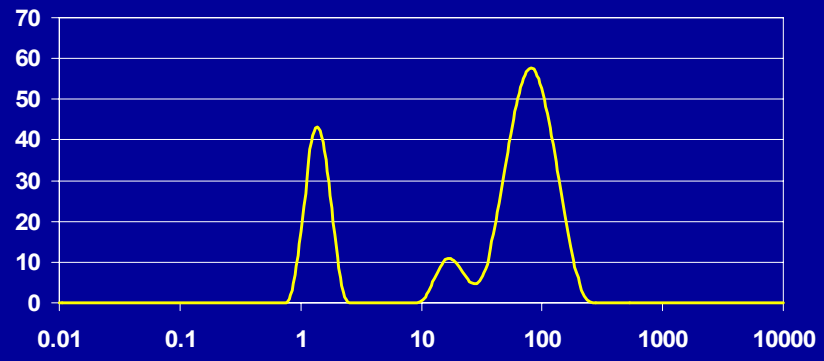


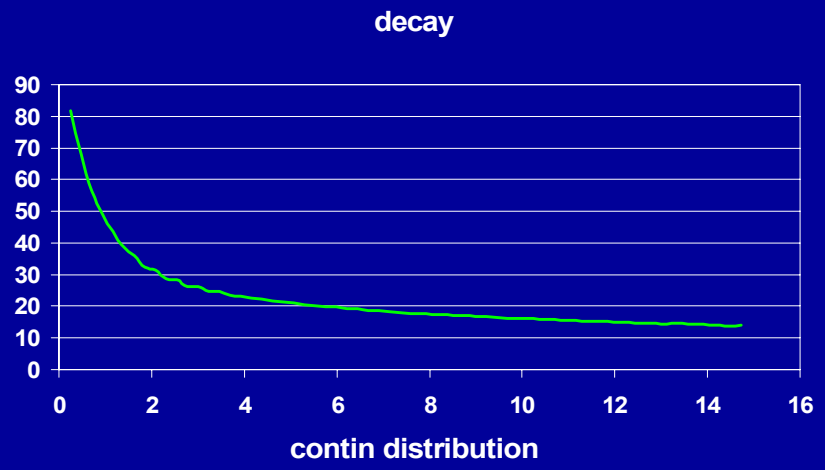


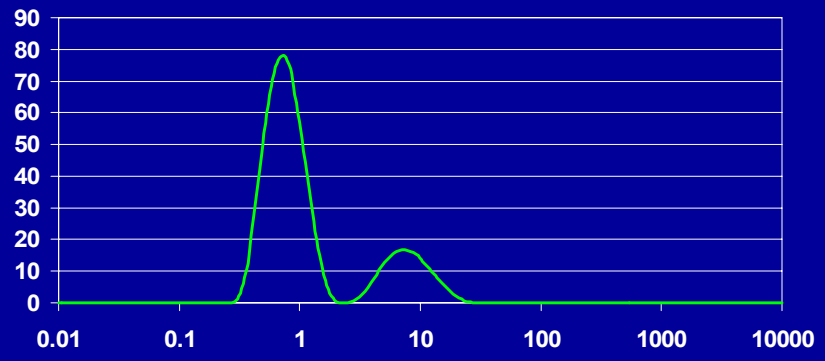


Furfuryl Alcohol







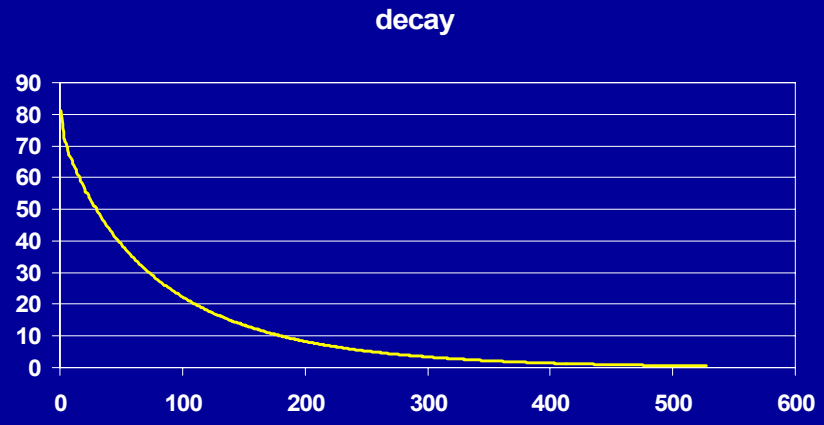


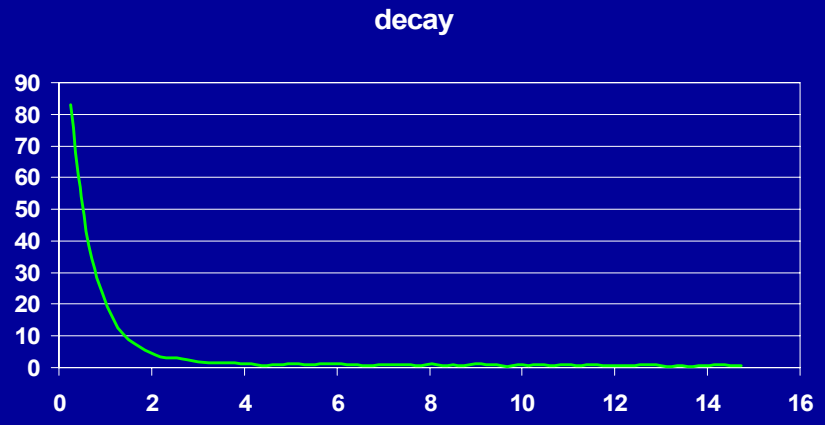
- Decay curve is still exponential
- Free water distribution is not as well-resolved
- The bound water is relaxing more rapidly (T2(1) is shorter)

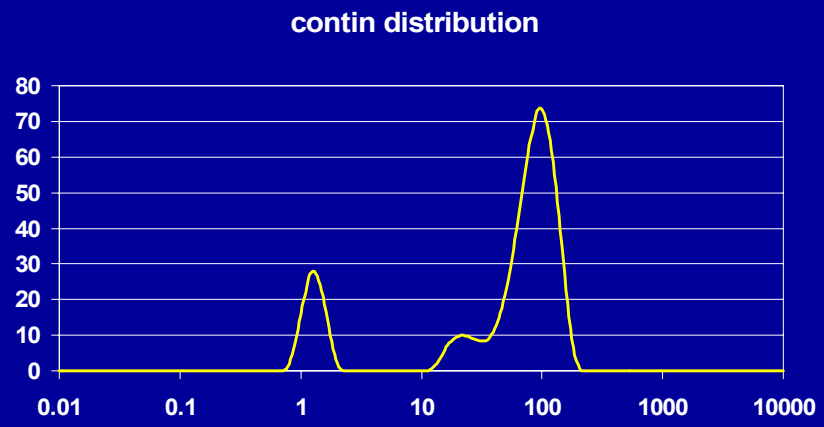
- Incomplete decay
- Longer relaxing peak (~10ms)
  - may be an artifact of the incomplete decay
  - May be FA itself or water bound to FA

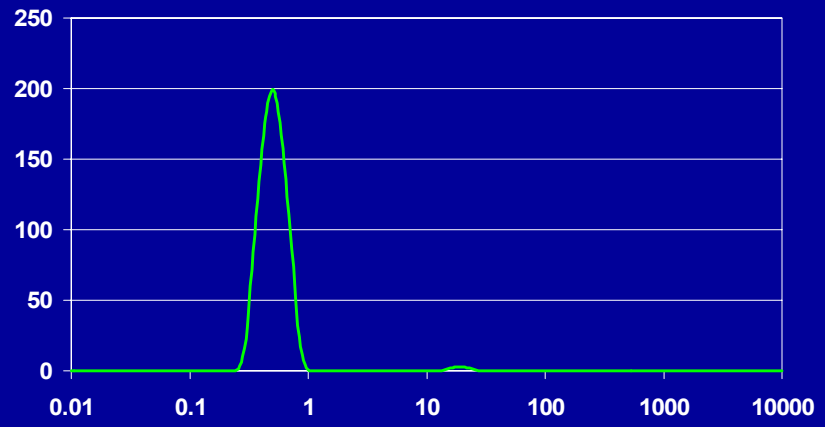
Furfuryl alcohol+ citric acid (low)

- Decay curve remains exponential
- Resolution in free water continues to degrade



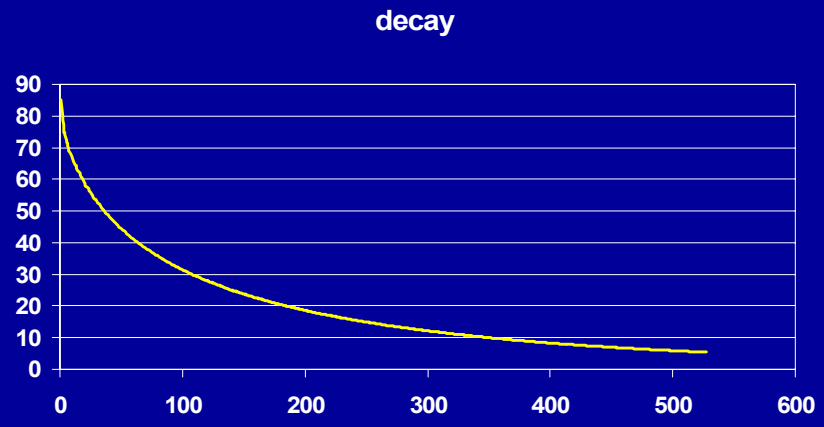


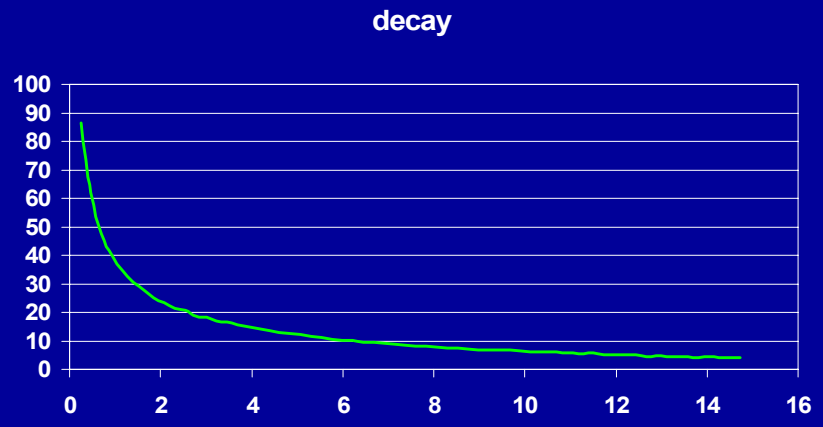


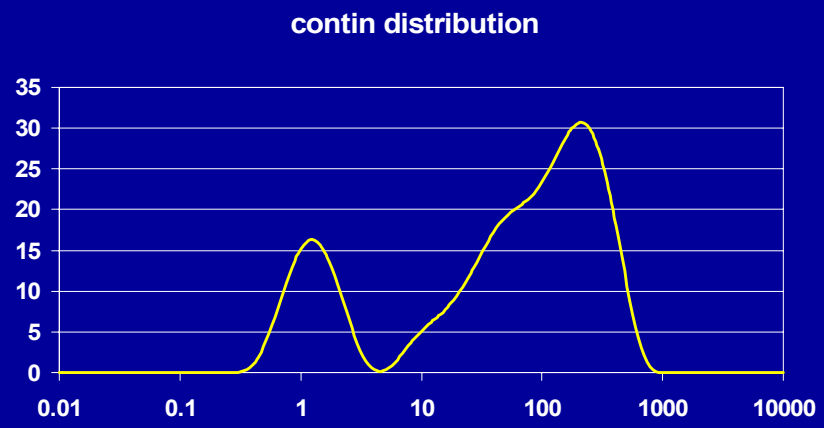


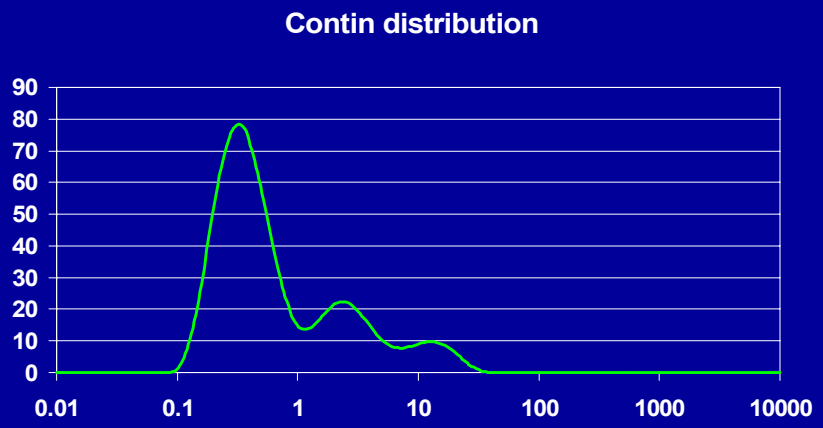
Furfuryl alcohol+ citric acid (high)

- The initial part of the decay curve is reasonably well-behaved, but neither sample completely decays
- The bound water peak for the saturated sample is much broader and the relaxation time is shorter
- The free water is very poorly resolved
- Multiple peaks in the sample at FSP



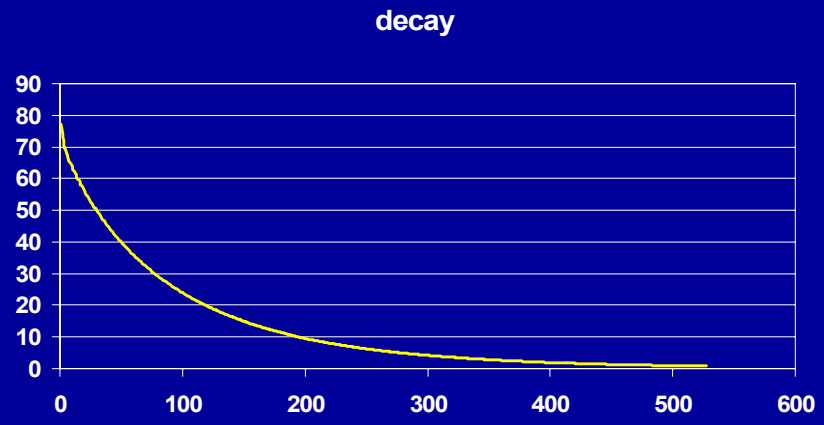


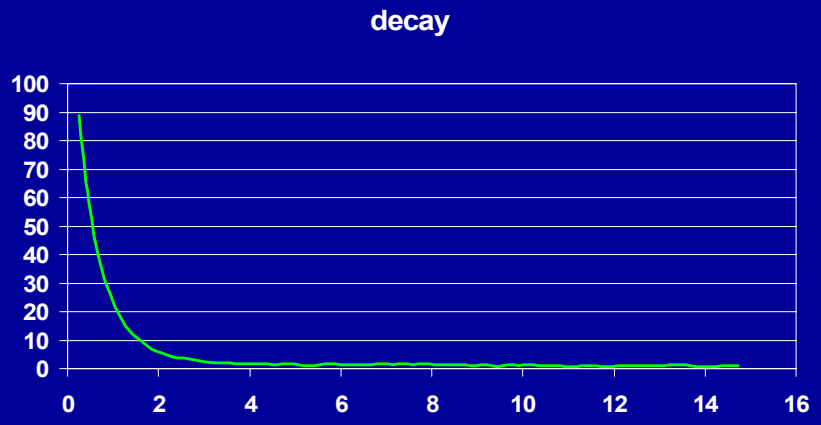


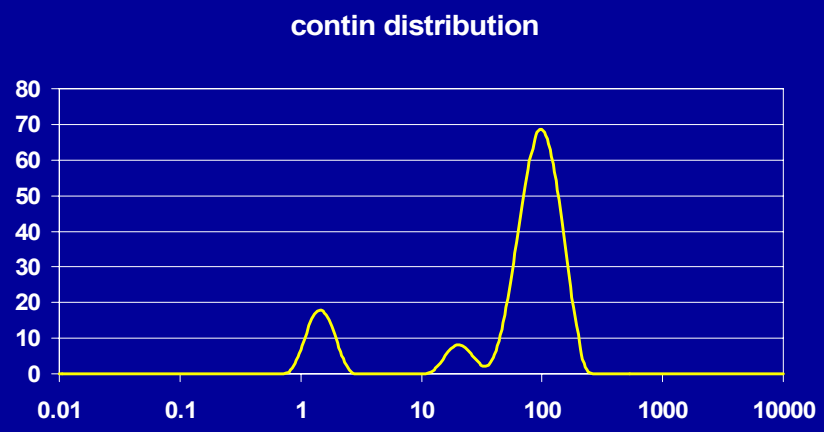


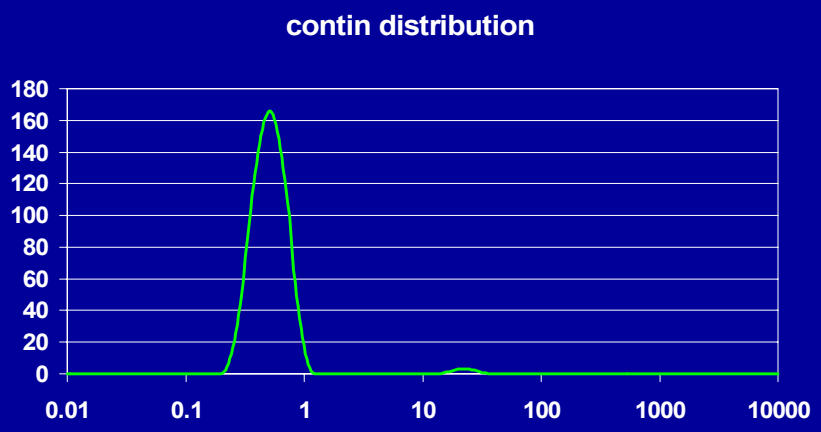
FA+CA+MA low

- Decay curves are typically exponential
- Bound water relaxation time is somewhat longer than previously observed
- Free water is fairly well-resolved.



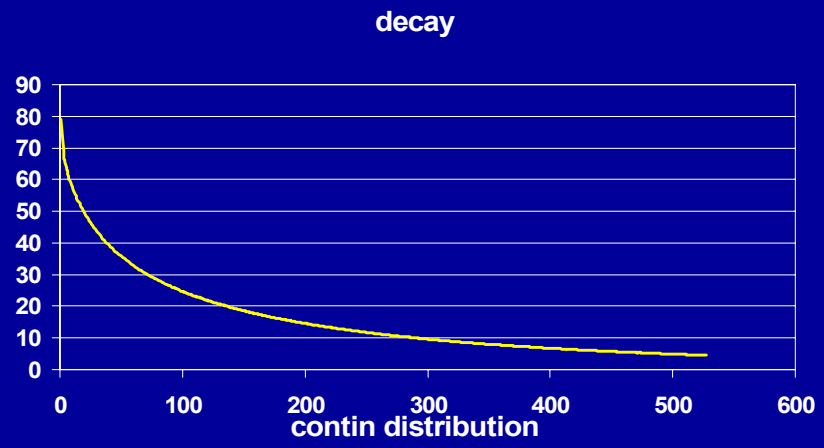


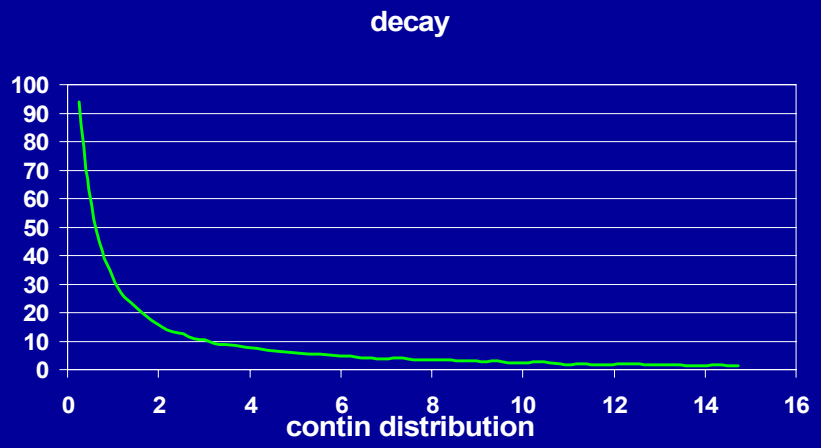


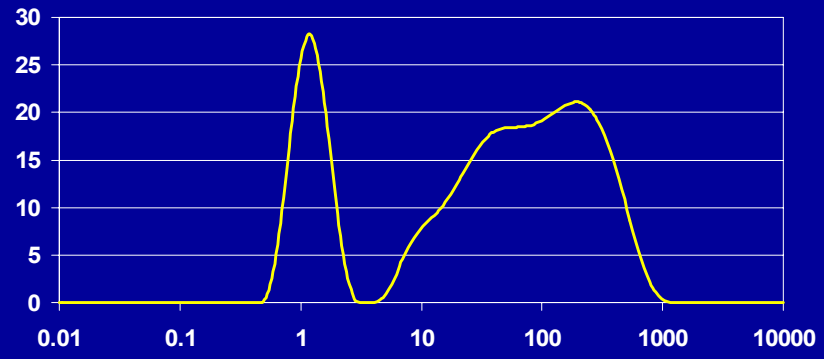


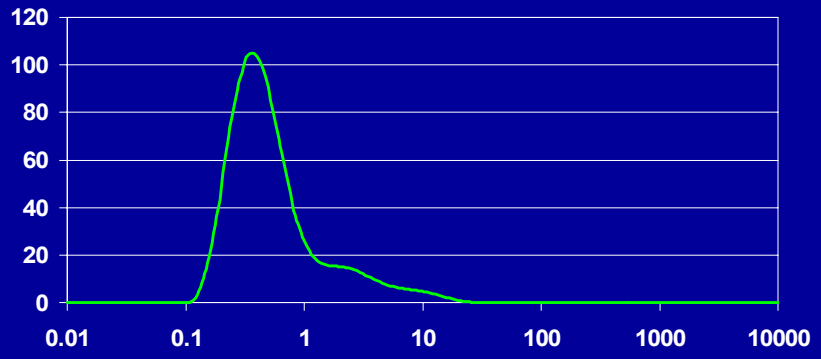
FA+CA+MA high

- Decay curve of saturated sample is similar to the FA+CA, high treatment, exhibiting incomplete decay.
- Poor resolution in free water
- Bound water amplitude is higher for the saturated sample
- Sample at FSP shows reasonable decay, but shoulder at longer T2



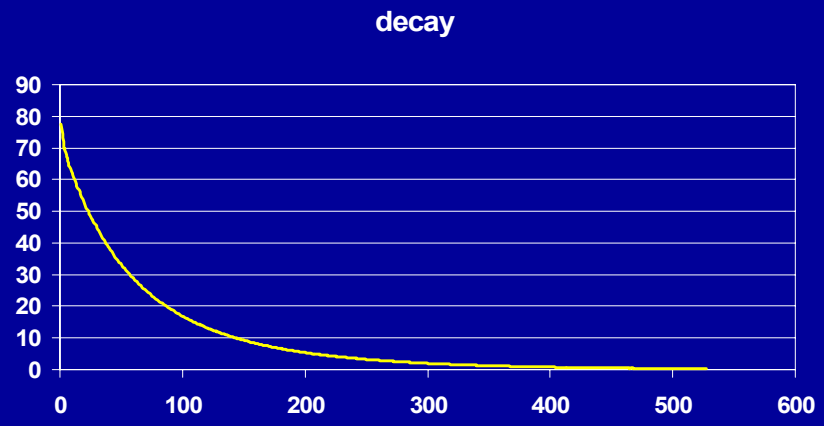


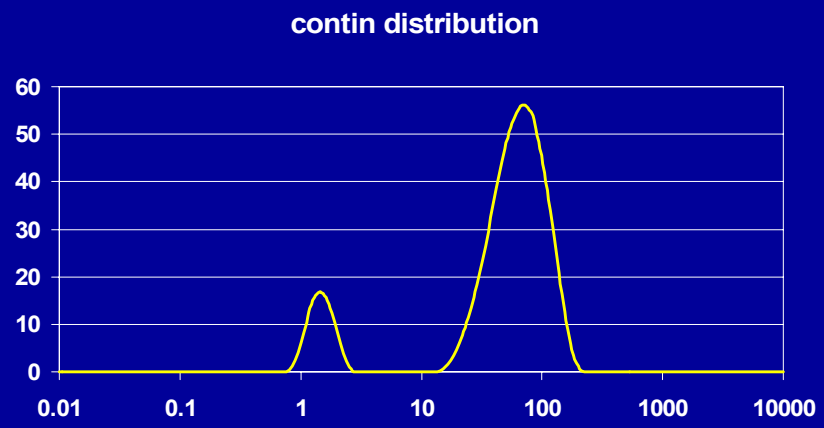


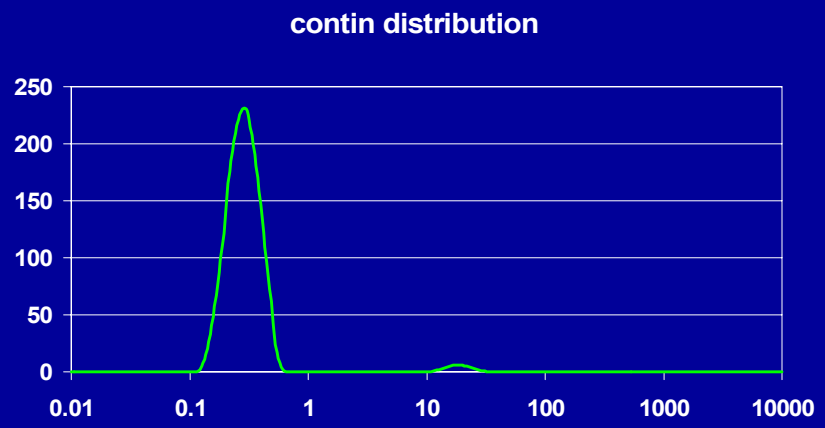


WPT

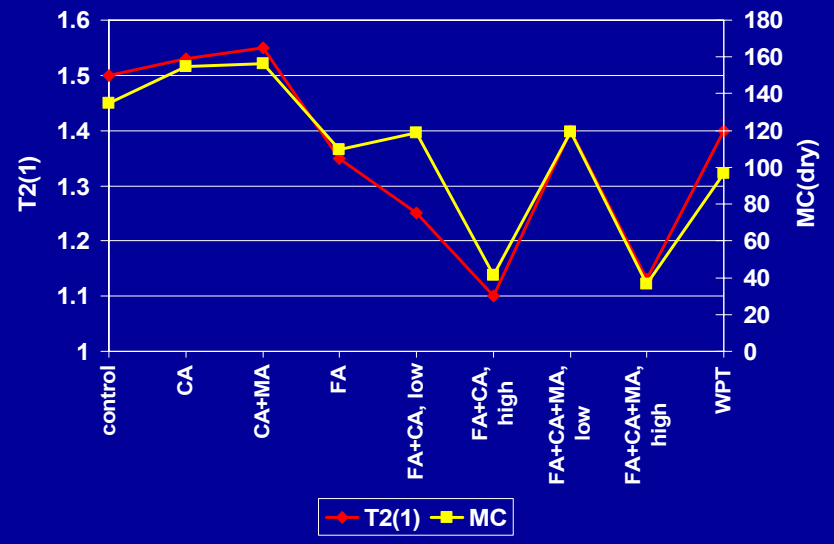
- Typical exponential decay curve
- Somewhat longer relaxation time for bound water
- Only one free water peak

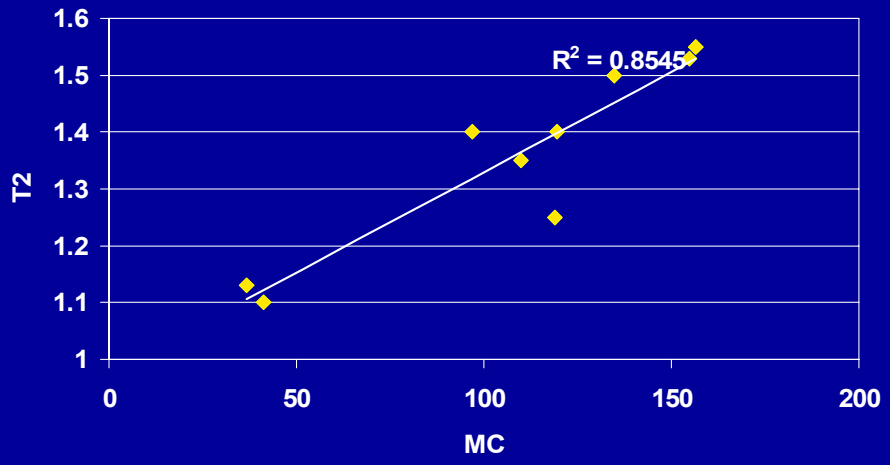






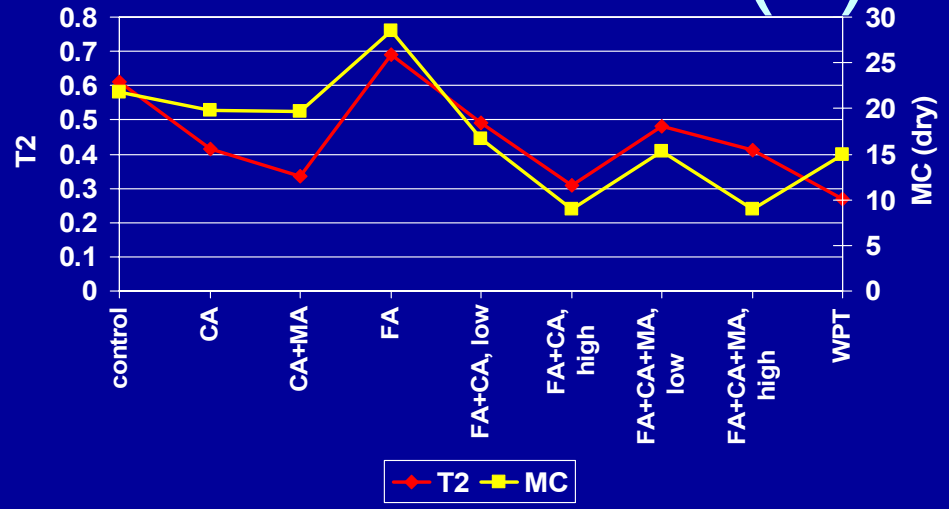
Saturated samples
Contin T2(1) values and MC

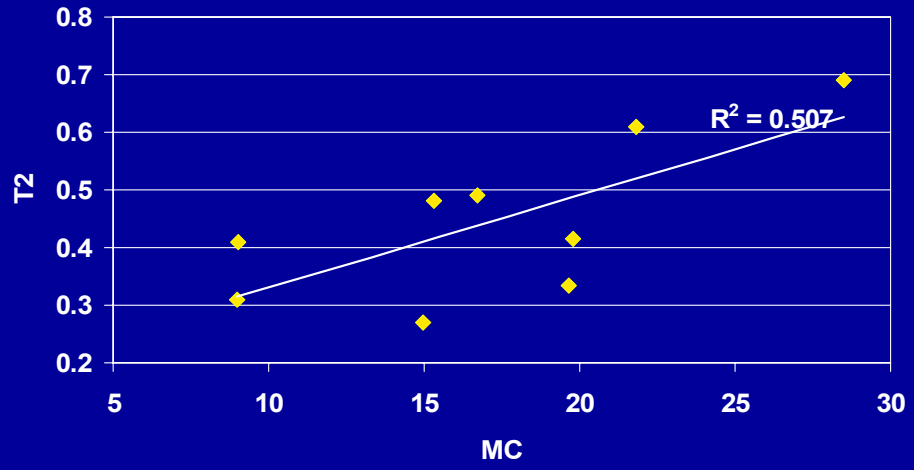




- As might be expected moisture contents markedly changed with treatment
- Inclusion of FA consistently lowered MC, particularly at high weight gains
- T2 and MC correspond closely

Samples at FSP
Contin T2(1) values and MC





- MC for these samples is also sensitive to treatment, and becomes quite low (~9%) with the high weight gain treatments
- As before MC and T2 correspond fairly well.

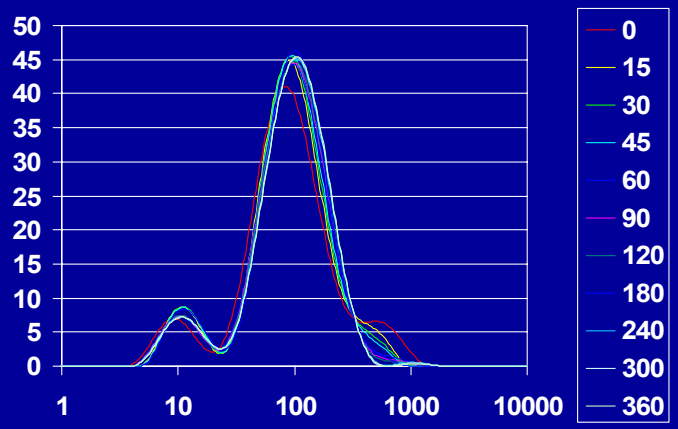
Results and Conclusions

- Weight gain occurs with the inclusion of FA
- LF-TD-NMR, shows decreased relaxation times for free water (which correlate well with moisture content) indicating lower levels of free water (reduction in “pools” of water)

Enzyme-cellulose-water studies

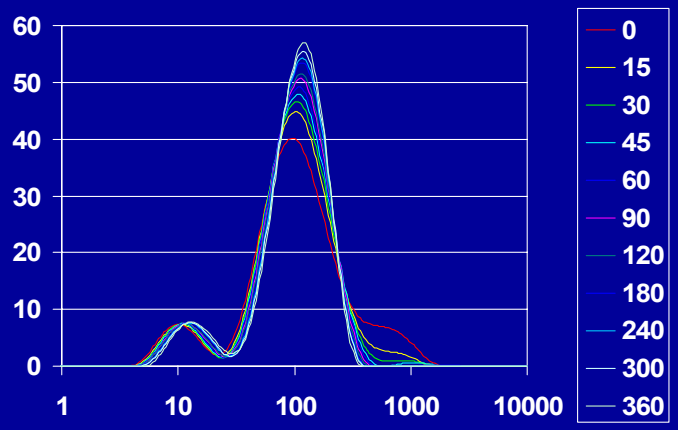
- Hypothesis
  - Cellulase enzymes bind to cellulose surfaces displacing bound water
- 1 g of Whatmann # 1 filter paper
- 2 g of buffer with or without enzyme(s)
  - Control –just buffer
  - 5 mg protein endohydrolase T. *longibrachiatum* (EG)
  - 5 mg protein cellobiohydrolase T. *longibrachiatum* (CBH)
  - 10 mg protein Celluclast (Novozymes)
- Allowed to soak for 5 min
- *No mechanical mixing!*
- NMR recorded from 0 to 360 min.

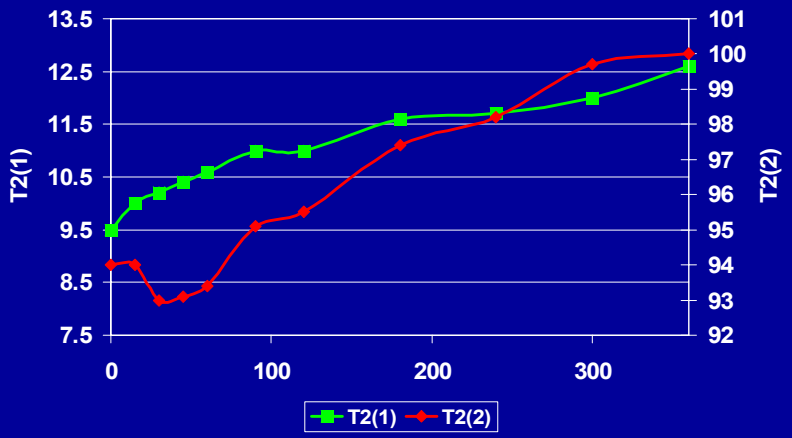
Control



- Bound water (~10ms) and free water (~100ms) are readily apparent.
- There is also a small shoulder just below 1000ms that disappears over time.
  - This is probably “bulk” water that is being adsorbed as the experiment progresses
  - Relaxation times of bound and free water increase initially and then remain fairly constant

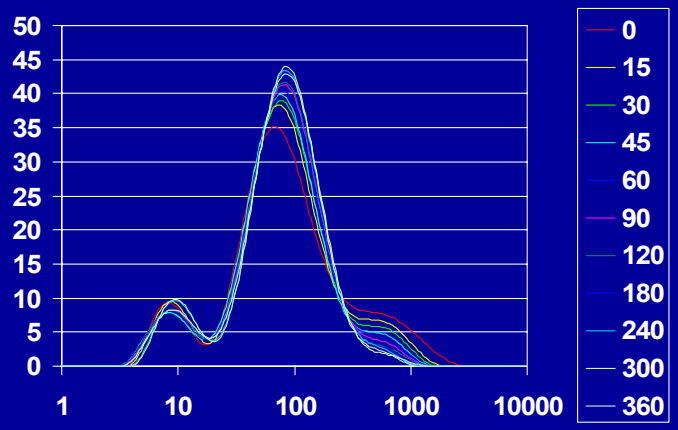
Endoglucanase

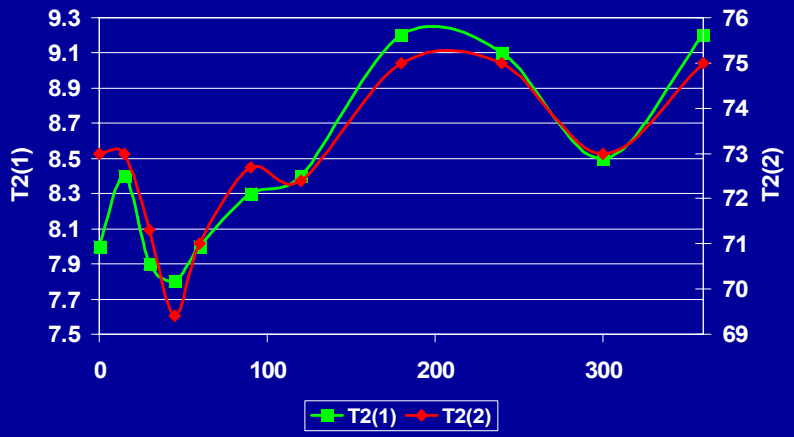




- Both bound and free water relaxation times increase with time

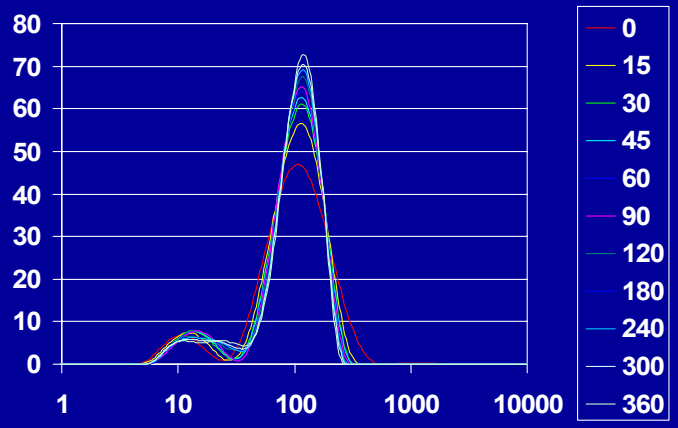
Cellobiohydrolase

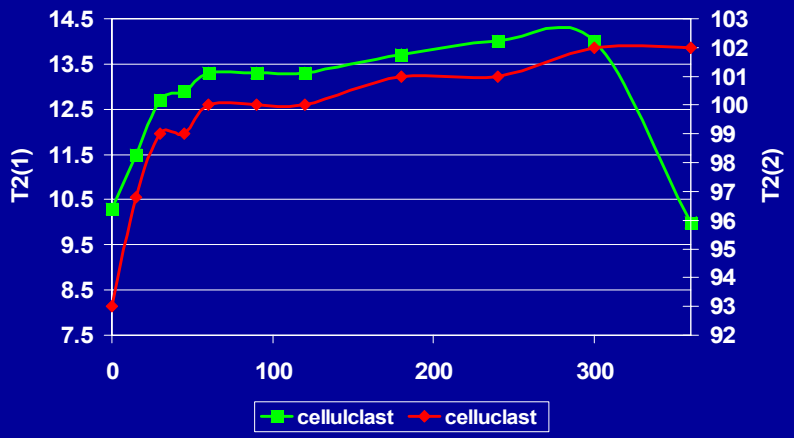




- Bound and free water T2s fluctuate over a narrow range

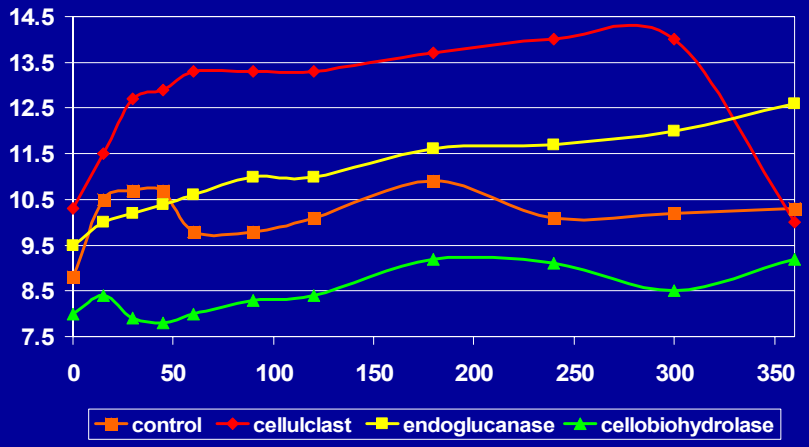
Celluclast





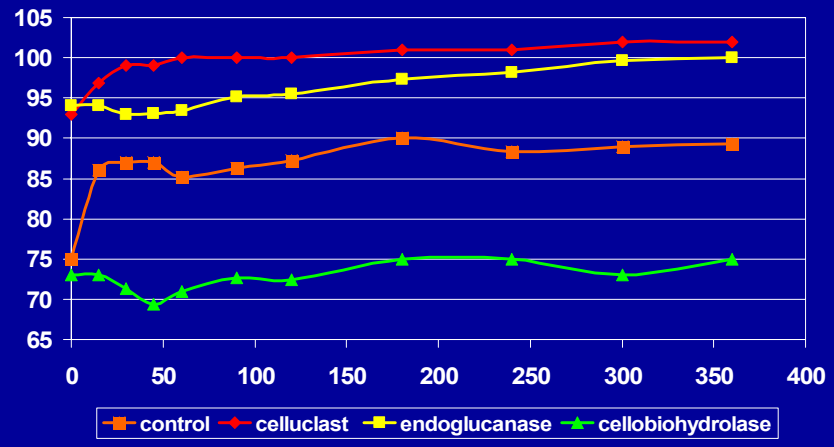
- After an initial rapid increase, both bound and free water relaxation times increase slightly with time

Comparison of bound water T2s



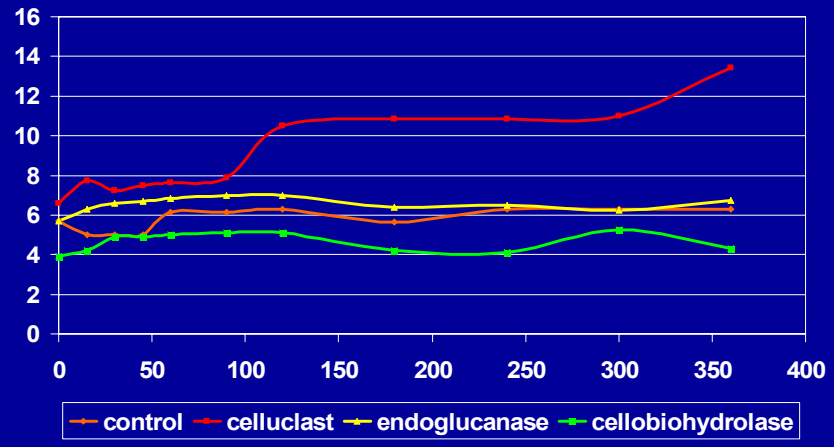
- In general, relaxation times for endoglucanase and cellulclast are longer than control
- Cellobiohydrolase results in shorter relaxation times

Comparison of free water T2s



- More pronounced difference between endoglucanase/celluclast and control/CBH
- Free water is relaxing more slowly with treatment and time.
  - This could be due to an increase in “bulk” water or an increase in porosity

A2/A1



- Ratios of amplitudes indicates that the relative amount of free water increases with celluclast treament
- Very small difference between control and endoglucanase

Results

- The relaxation times for bound water (T2(1)) do not vary much and don't show much in terms of patterns between the treatments. Although the control is generally faster.
- The relaxation times for the free water (T2(2)) are similar for the enzyme treatment and both are longer than the control.
  - The longer relaxation times could mean
    - an increase in porosity due to the action of the enzyme
    - Simply interaction of the water with the enzyme
    - An increase in of free water (?)

Other completed and ongoing studies

- Charcoal
- Cellulose treated in electron beam
- Effect of pre-treatment on biomass
- Detection of extractives
- Thermal treatment of MDF furnish