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Monitoring Acid-Catalyzed Hydrolysis of Sucrose Through Low-Resolution NMR Relaxometry

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NMR Relaxometry ? MRI in Foods?

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REVIEW ARTICLE

^{1}H Nuclear Magnetic Resonance Relaxometry and Magnetic Resonance Imaging and Applications in Food Science and Processing

Emrah Kirtil[1] · Mecit H. Oztop[1]

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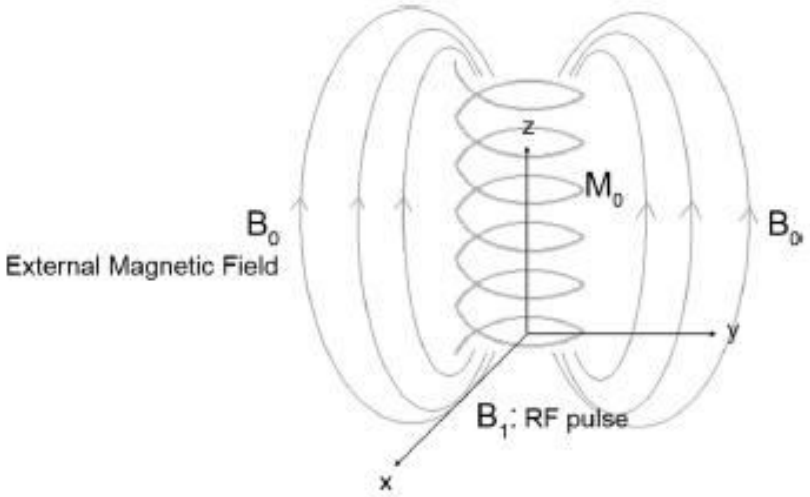


Fig. 1 Schematic of magnetization occurred by placing a sample into an external magnetic field in z direction (B_0)

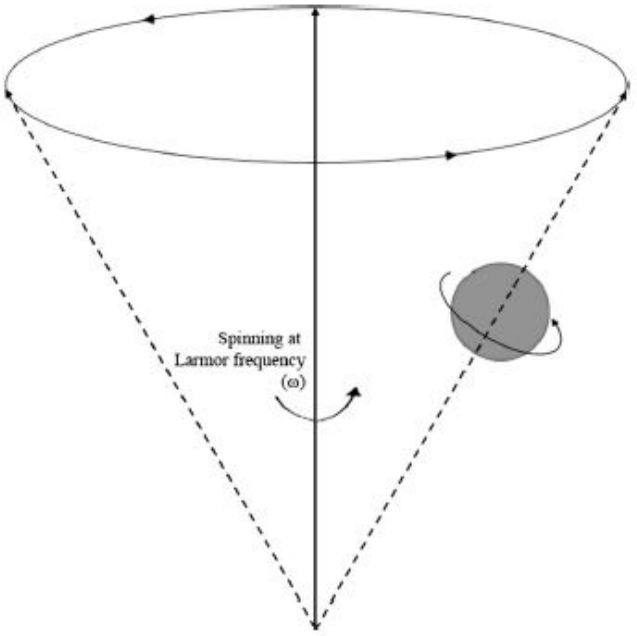
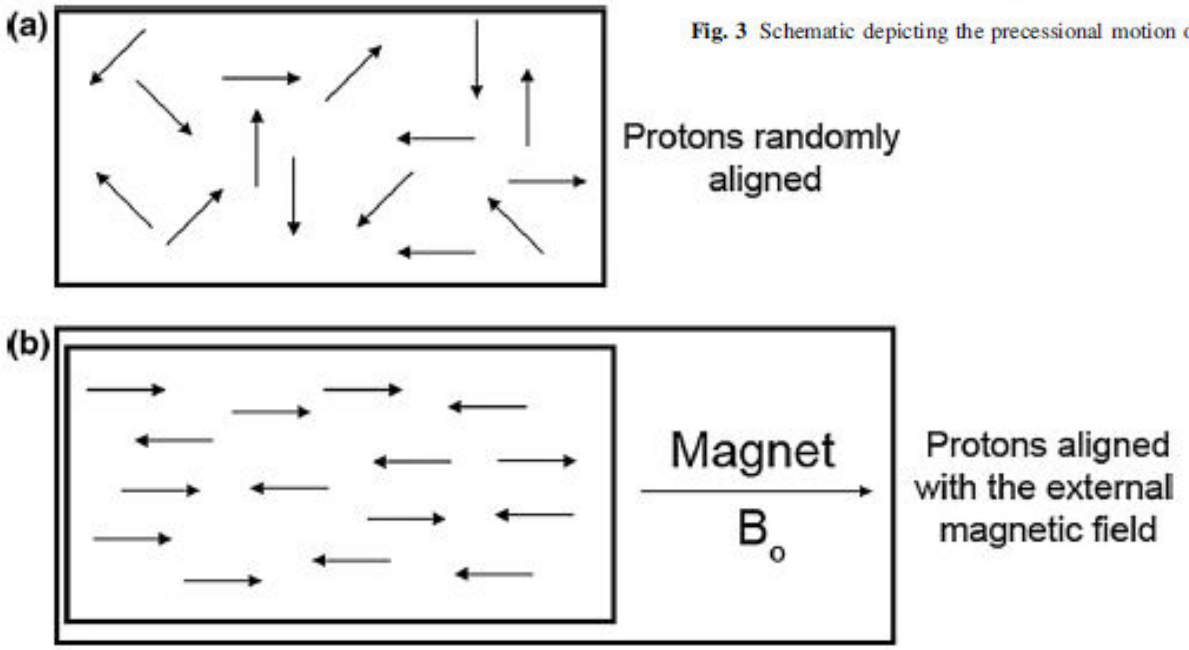


Fig. 3 Schematic depicting the precessional motion of protons

Fig. 2 Schematic showing the direction that protons are facing in samples. **a** Without the presence of an external magnetic field, **b** under the influence of an external magnetic field of B_0



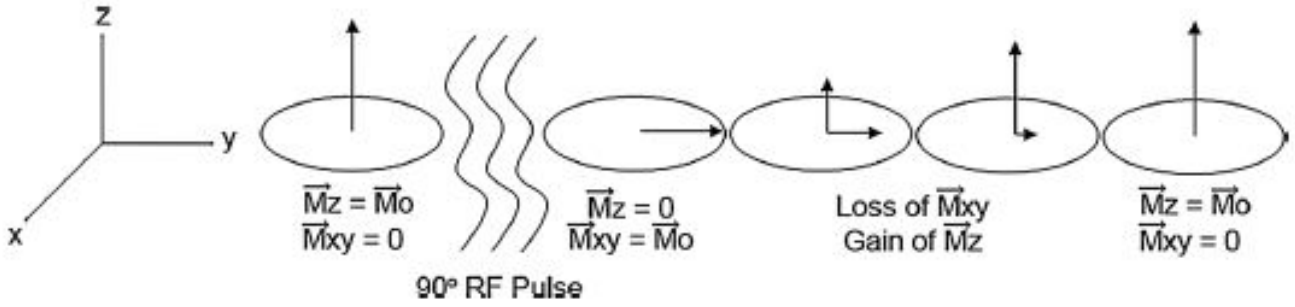


Fig. 5 Relaxation of transverse (M_{xy}) and longitudinal (M_z) magnetization after application of a 90° RF pulse

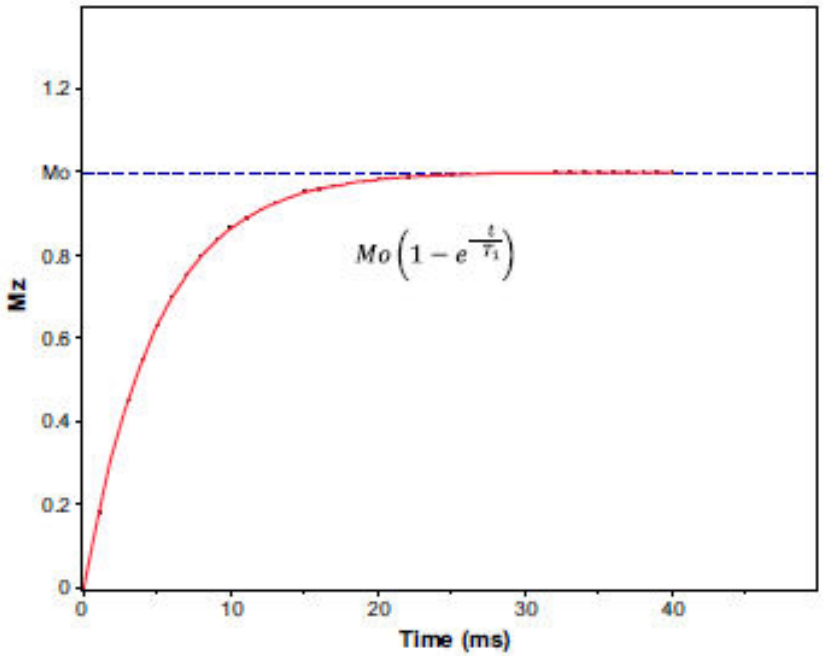


Fig. 6 A representative exponential relaxation curve of longitudinal magnetization for a sample with a T_1 of 10 ms

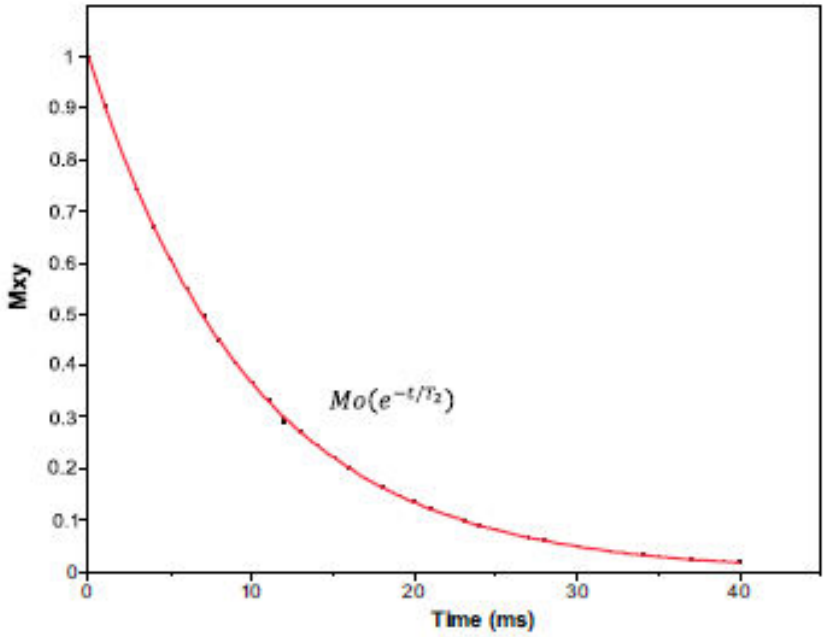
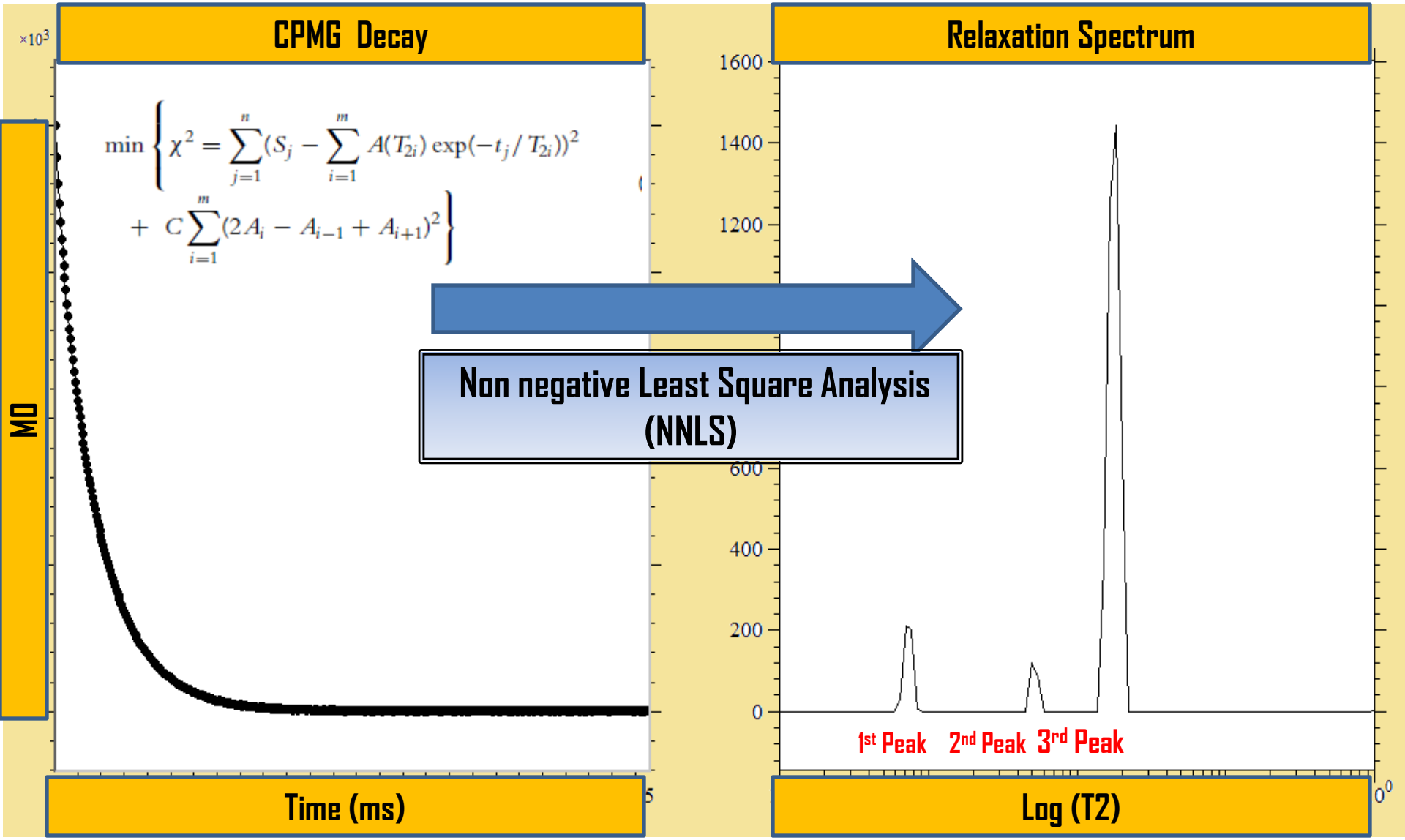


Fig. 7 A representative exponential relaxation curve of transversal magnetization for a sample with a T_2 of 10 ms

Spin-spin Relaxation Time -T_2- Relaxation Spectrum



Magnetic Resonance Imaging (MRI) and Relaxation Spectrum Analysis as Methods to Investigate Swelling in Whey Protein Gels

Mecit H. Oztop, Moshe Rosenberg, Yael Rosenberg, Kathryn L. McCarthy, and Michael J. McCarthy

Characterization of Water Distribution in Xanthan-Curdlan Hydrogel Complex Using Magnetic Resonance Imaging, Nuclear Magnetic Resonance Relaxometry, Rheology, and Scanning Electron Microscopy

Patrick D. Williams, Mecit Halil Oztop, Michael J. McCarthy, Kathryn L. McCarthy, and Y. Martin Lo

Disintegration Efficiency of Pulsed Electric Field Induced Effects on Onion (*Allium cepa* L.) Tissues as a Function of Pulse Protocol and Determination of Cell Integrity by ^{1}H-NMR Relaxometry

Seda Ersus, Mecit Halil Oztop, Michael J. McCarthy, and Diane M. Barrett

Effect of pectin methyl esterase (PME) and $CaCl_2$ infusion on the cell integrity of fresh-cut and frozen-thawed mangoes: An NMR relaxometry study

Emrah Kirtil [a], Mecit H. Oztop [a,*], Arpassorn Sirijariyawat [c], Panita Ngamchuachit [c,d], Diane M. Barrett [b], Michael J. McCarthy [b]

Monitoring the effects of divalent ions (Mn^{+2} and Ca^{+2}) in heat-set whey protein gels

Mecit H. Oztop [a,c,*], Kathryn L. McCarthy [a,b], Michael J. McCarthy [a,b], Moshe Rosenberg [b]

Whey protein/alginate beads as carriers of a bioactive component

S. Wichchukit [a,b], M.H. Oztop [e], M.J. McCarthy [c,d], K.L. McCarthy [c,d,*]

Uptake of Divalent Ions (Mn^{+2} and Ca^{+2}) by Heat-Set Whey Protein Gels

Mecit H. Oztop, Kathryn L. McCarthy, Michael J. McCarthy, and Moshe Rosenberg

Effect of boiling, roasting and frying on disintegration of peanuts in simulated gastric environment

Fanbin Kong [a], Mecit Halil Oztop [b,e], R. Paul Singh [b,c,*], Michael J. McCarthy [b,d]

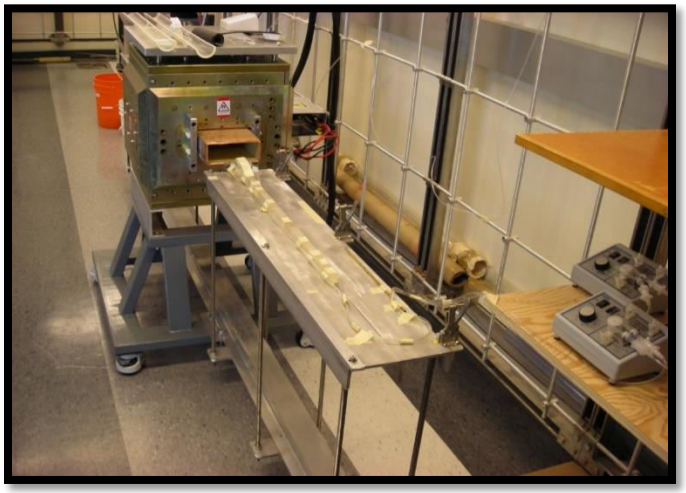
Physical Changes in White and Brown Rice during Simulated Gastric Digestion

Fanbin Kong, Mecit Halil Oztop, R. Paul Singh, and Michael J. McCarthy

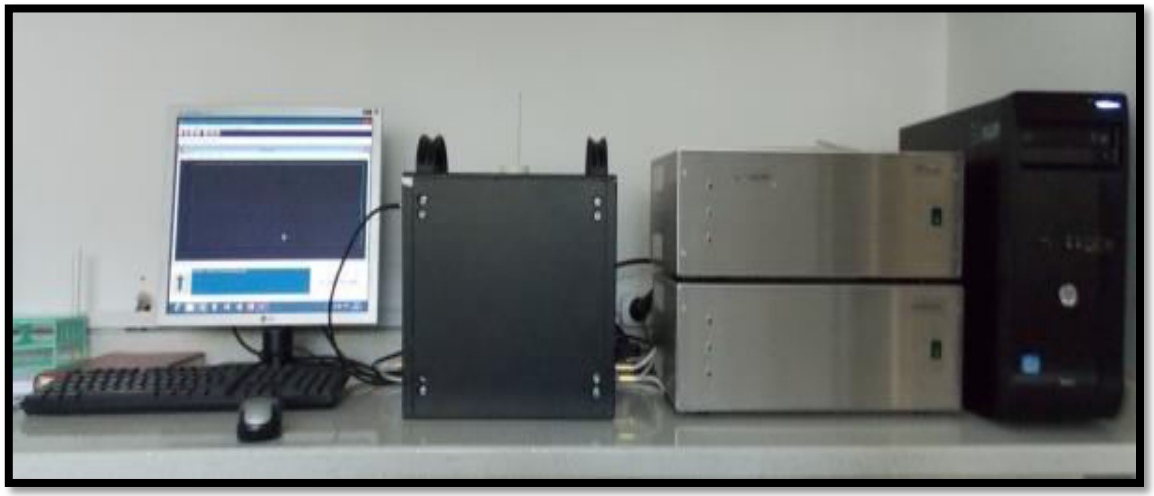
Monitoring changes in feta cheese during brining by magnetic resonance imaging and NMR relaxometry

Aylin Altan [a,d], Mecit H. Oztop [b,c], Kathryn L. McCarthy [a,b], Michael J. McCarthy [a,b,*]

1 Tesla



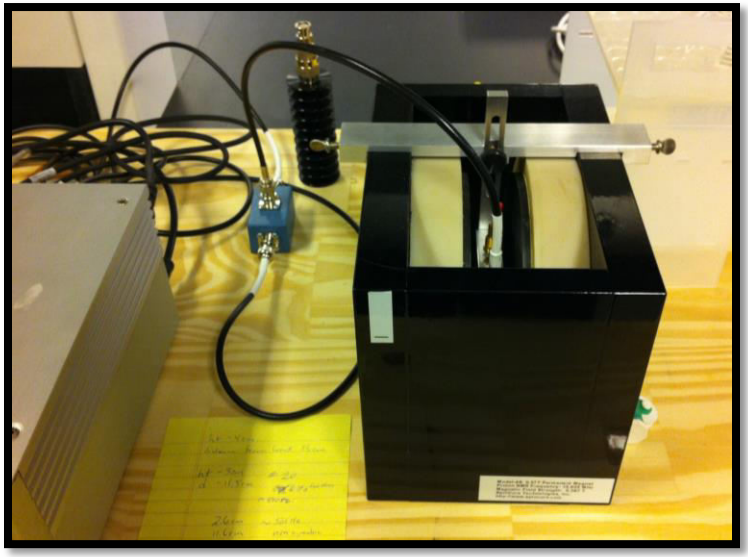
0.32 Tesla

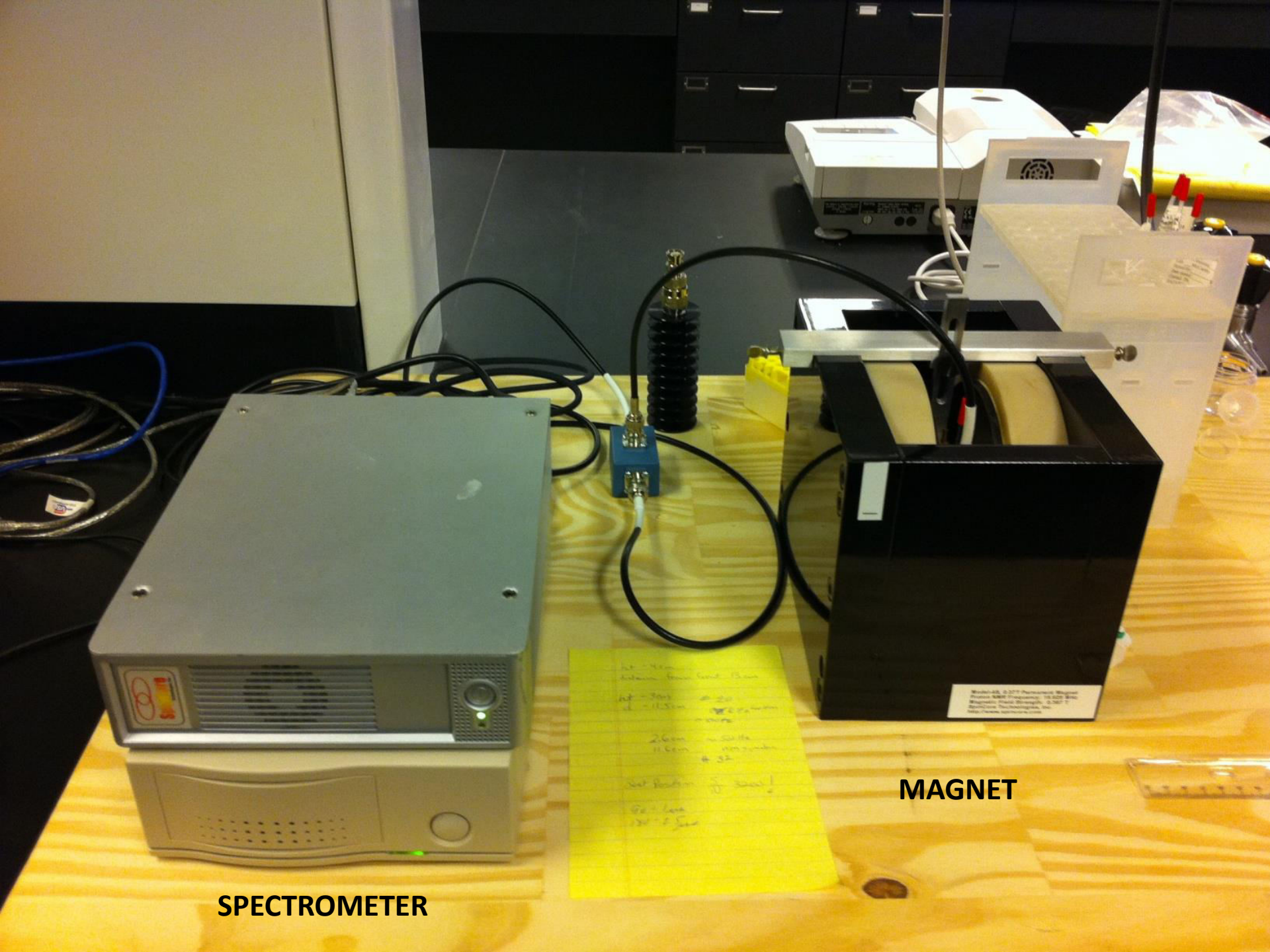


3 Tesla



0.5 Tesla




MAGNET
SPECTROMETER

Monitoring Chemical Reactions

Many analytical techniques (IR, UV, Raman) are used to monitor chemical reactions.

–For many reactions these techniques show important features of the reaction process and therefore provide a great deal of information to apply to a process

What type of NMR experiments are talking?

•On-line NMR is a very powerful tool for monitoring reaction progression as well as providing mechanistic insight into the synthesis.


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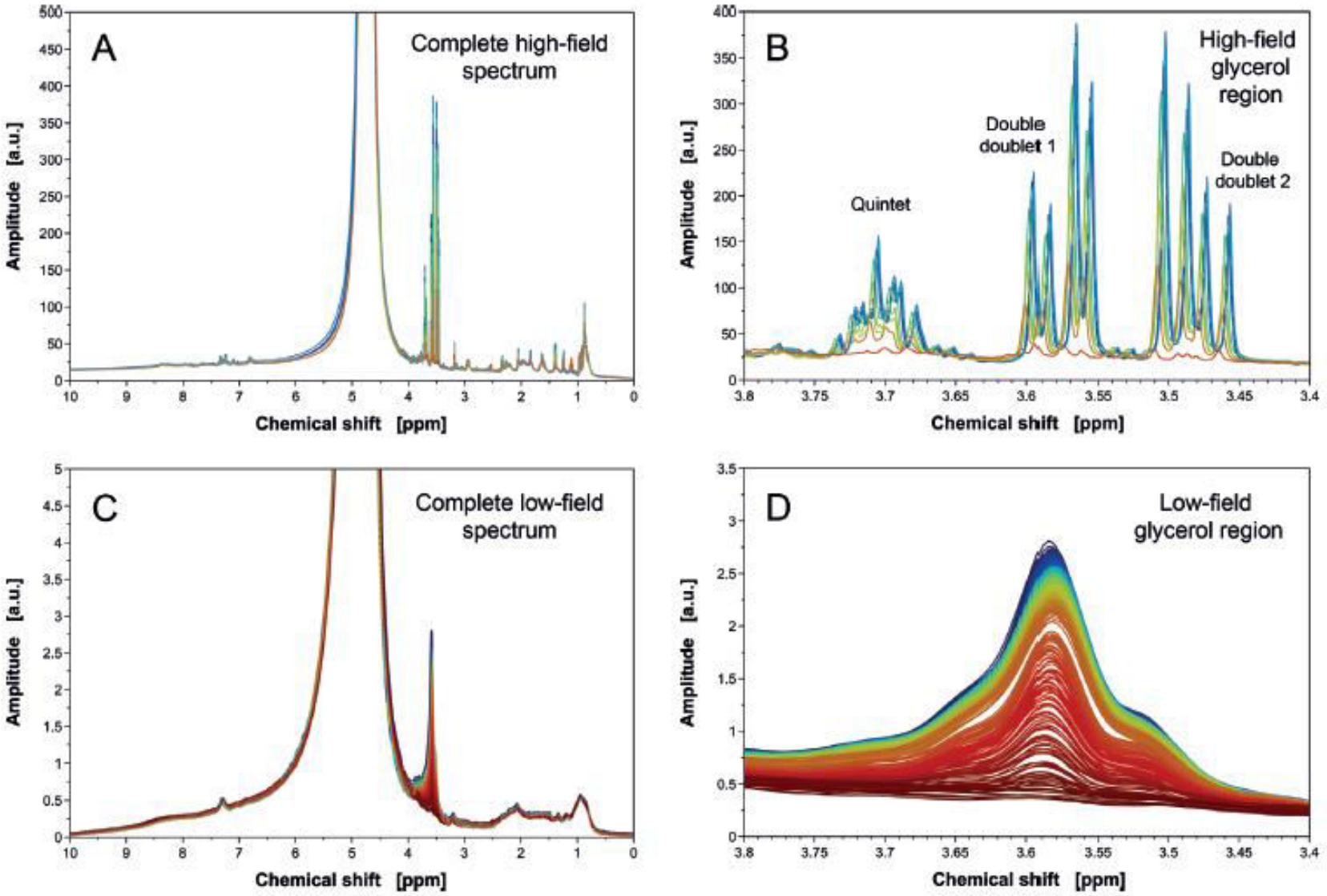


Figure 2. High-field and low-field ^{1}H NMR spectra of *Hansenula polymorpha* fermentation in complex medium. The color of the spectra indicates cultivation time with a dark blue for cultivation start and red for the end of the cultivation (23 h). High-field spectra (A and B) were acquired at 400 MHz from unfiltered samples taken at discrete time points during cultivation. Low-field spectra (C and D) were recorded non-invasively every 15 s in the external bypass. Twelve subsequent low-field scans were accumulated, respectively, yielding one spectrum every 3 min. (B and D) Spectral regions utilized for glycerol quantification.

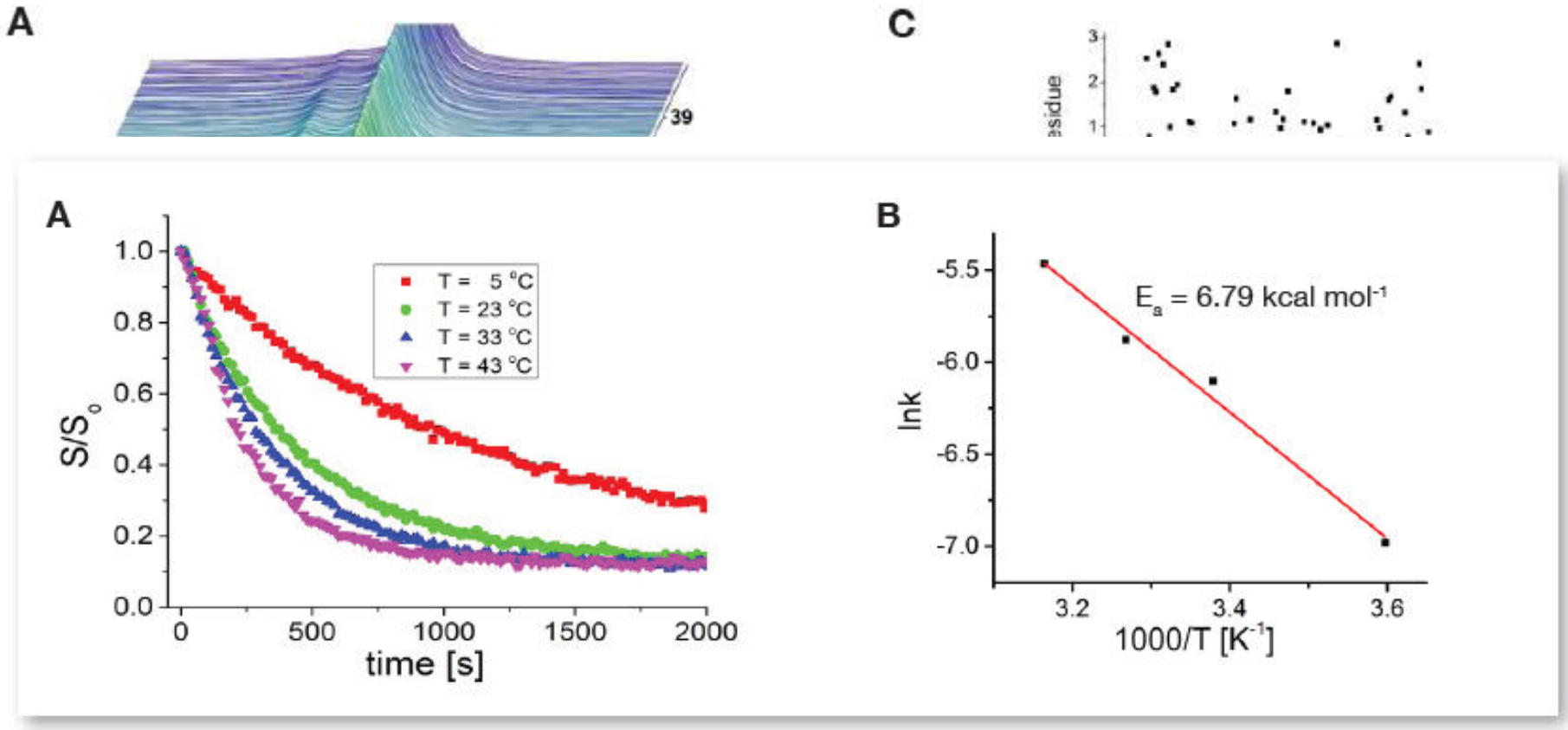
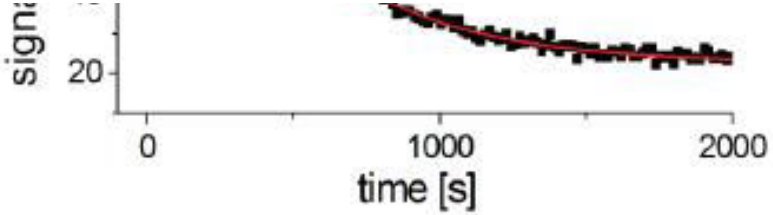


Figure 4. (A) Reaction profiles at various temperatures, showing the effect of temperature on the rate of the reaction (B) Arrhenius plot.



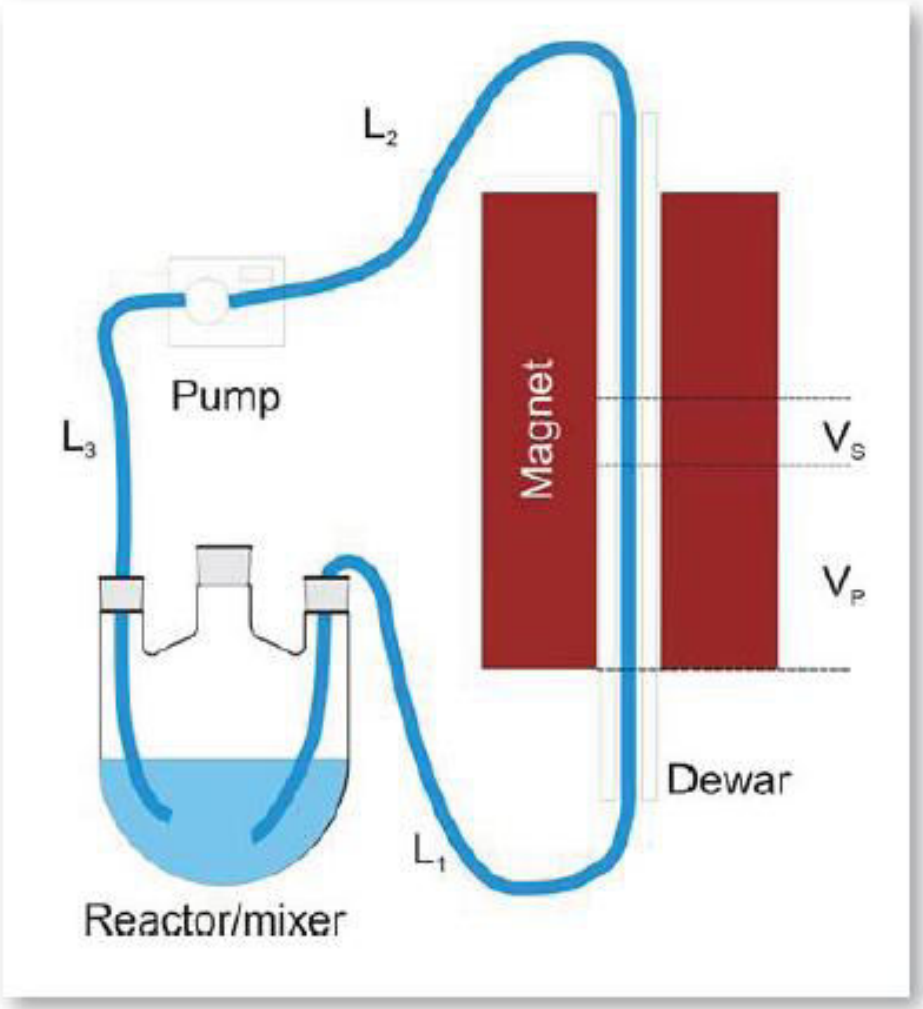


Figure 5: Flow Setup. The reaction mixture is pumped from the reactor to the magnet via L_1, from the magnet to the pump via L_2 and from the pump back to the reactor via L_3.



- Tubing type: PTFE
- Maximum OD: 2 mm
- Typical ID: 1.0-1.5 mm
- Typical Length: 3 m (L_1+L_2+L_3)
- Volume L1: 1.5 ml
- Total volume: 5 ml
- T_{max} reactor: 100°C
- T_{max} magnet: 30°C

What about Medium and Low-Resolution NMR ($\leq$0.5 T)?

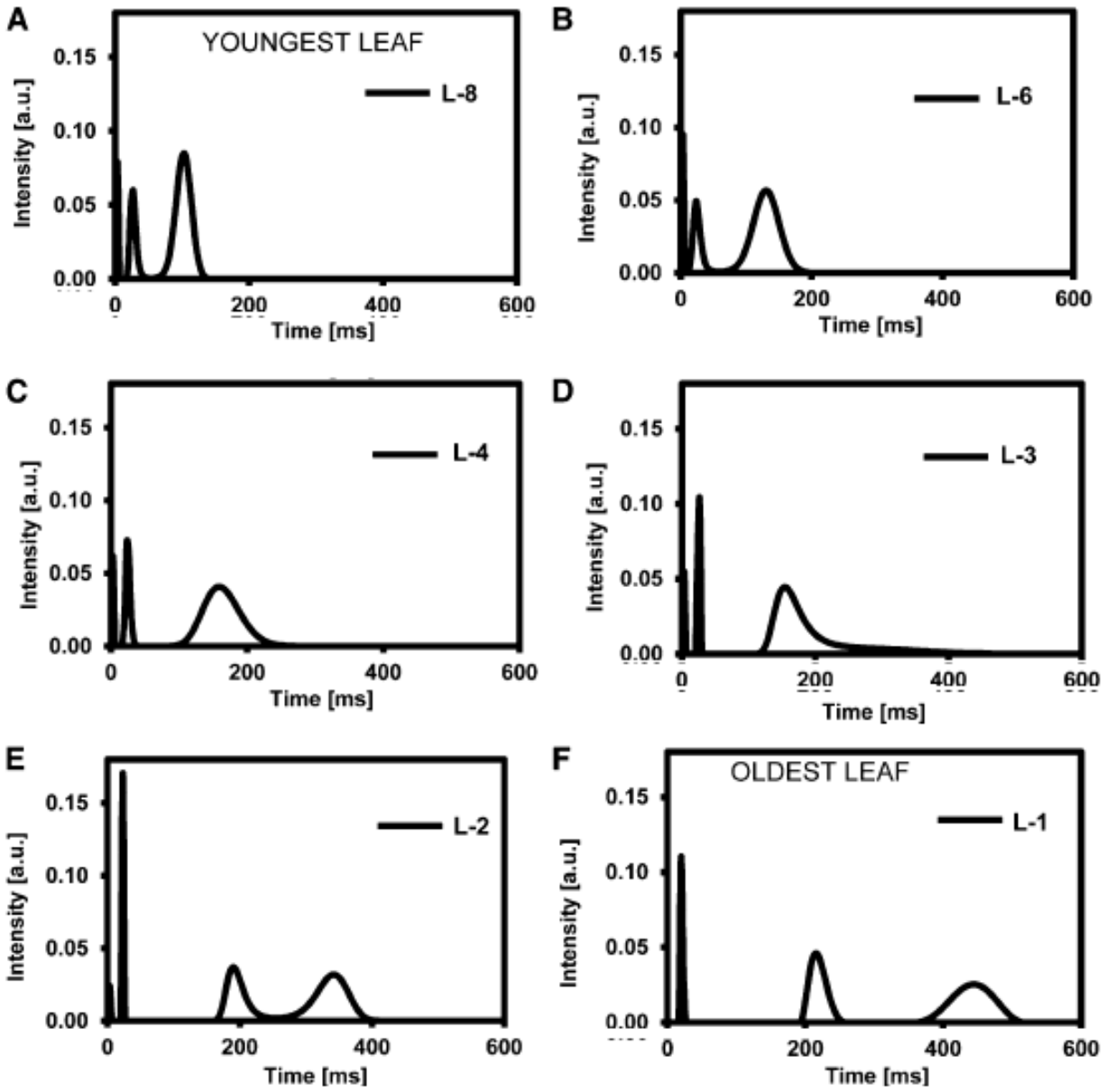


Figure 4. Transverse relaxation time distribution (MEM) calculated from the CPMG signal for oilseed rape leaves of six different leaf ranks (L). Data shown correspond to P-5.

Novel ^{1}H low field nuclear magnetic resonance applications for the field of biodiesel

Paula Berman[1], Adi Leshem[1], Oren Etziony[1], Ofer Levi[2], Yisrael Parmet[2], Michael Saunders[3] and Zeev Wiesman[1*]

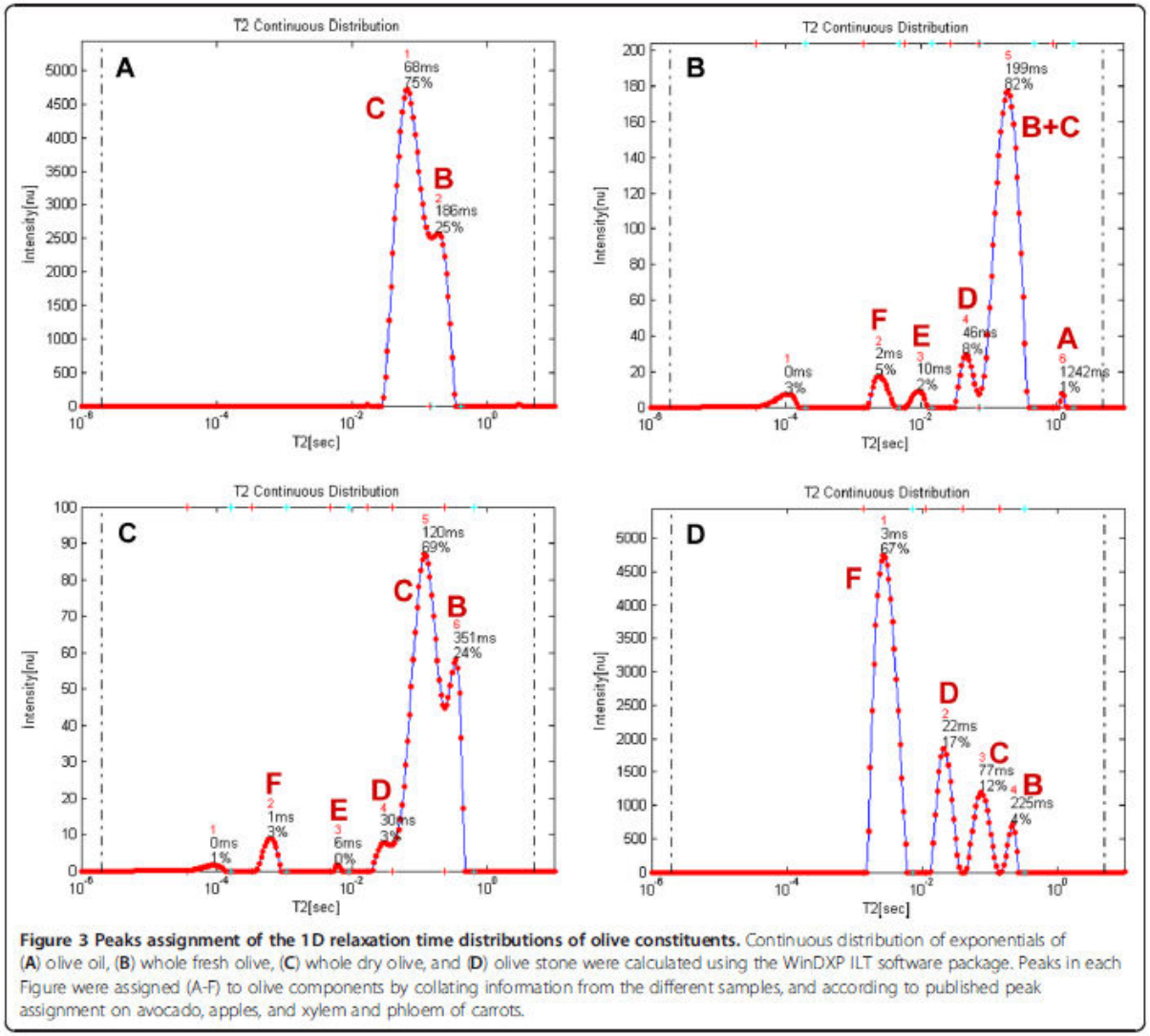


Figure 3 Peaks assignment of the 1D relaxation time distributions of olive constituents. Continuous distribution of exponentials of (**A**) olive oil, (**B**) whole fresh olive, (**C**) whole dry olive, and (**D**) olive stone were calculated using the WinDXP ILT software package. Peaks in each Figure were assigned (A-F) to olive components by collating information from the different samples, and according to published peak assignment on avocado, apples, and xylem and phloem of carrots.

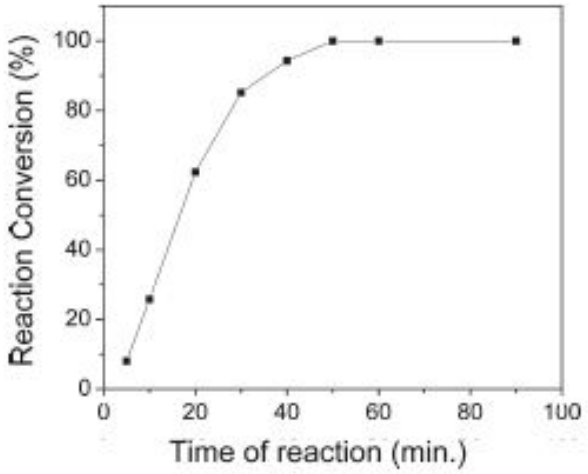


Figure 2. Biodiesel conversion at different reaction times calculated from the ^{1}H NMR spectra and eq 1.[19]

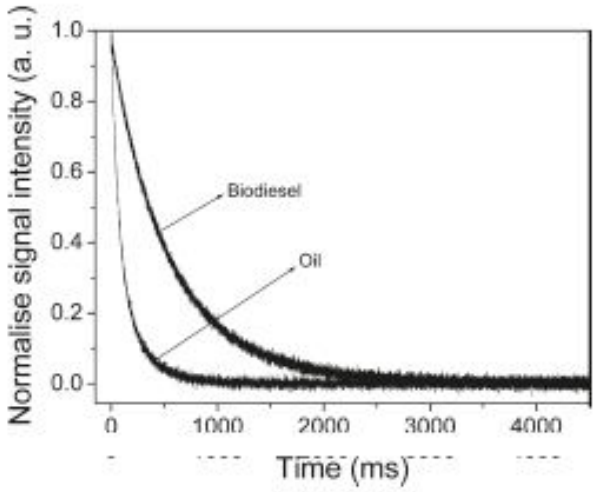


Figure 3. ^{1}H CPMG decay for soybean oil and biodiesel using a benchtop LRNMR spectrometer.

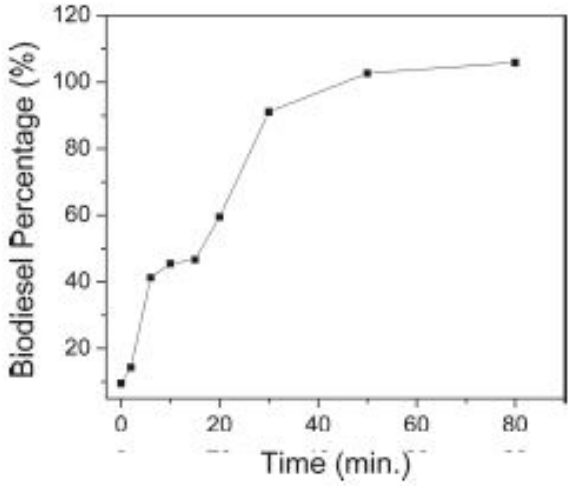


Figure 5. Biodiesel percentage produced by the transesterification reaction from 0 to 90 min and calculated by the CPMG decay and calibration curve of Figure 4.

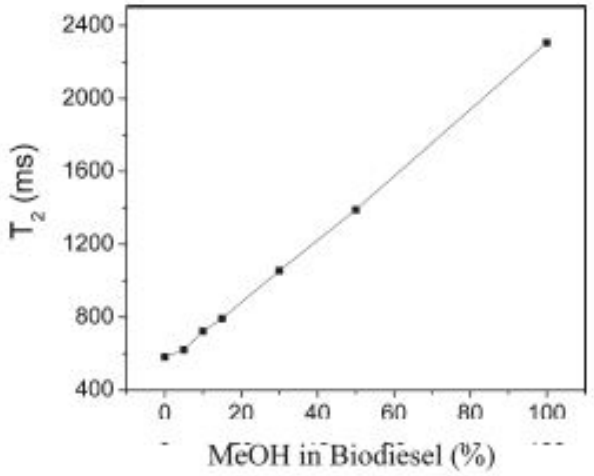
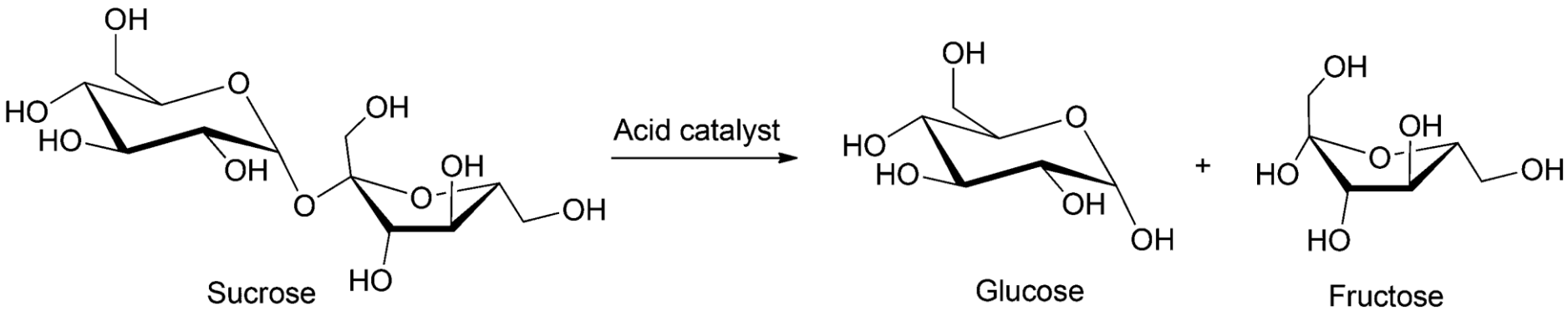


Figure 6. T_2 values for different methanol percentages in biodiesel using a benchtop LRNMR spectrometer.

What we did ?



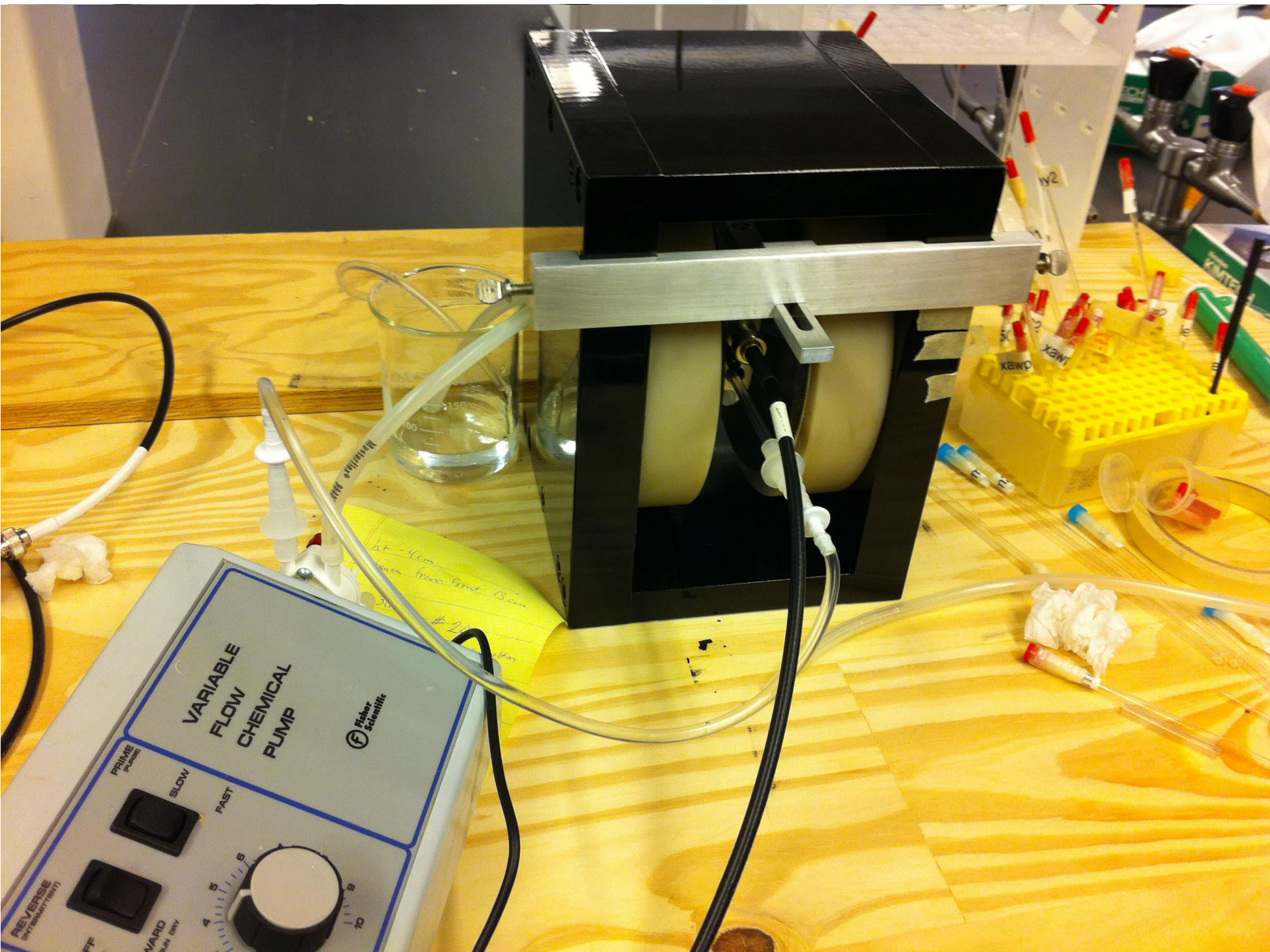
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

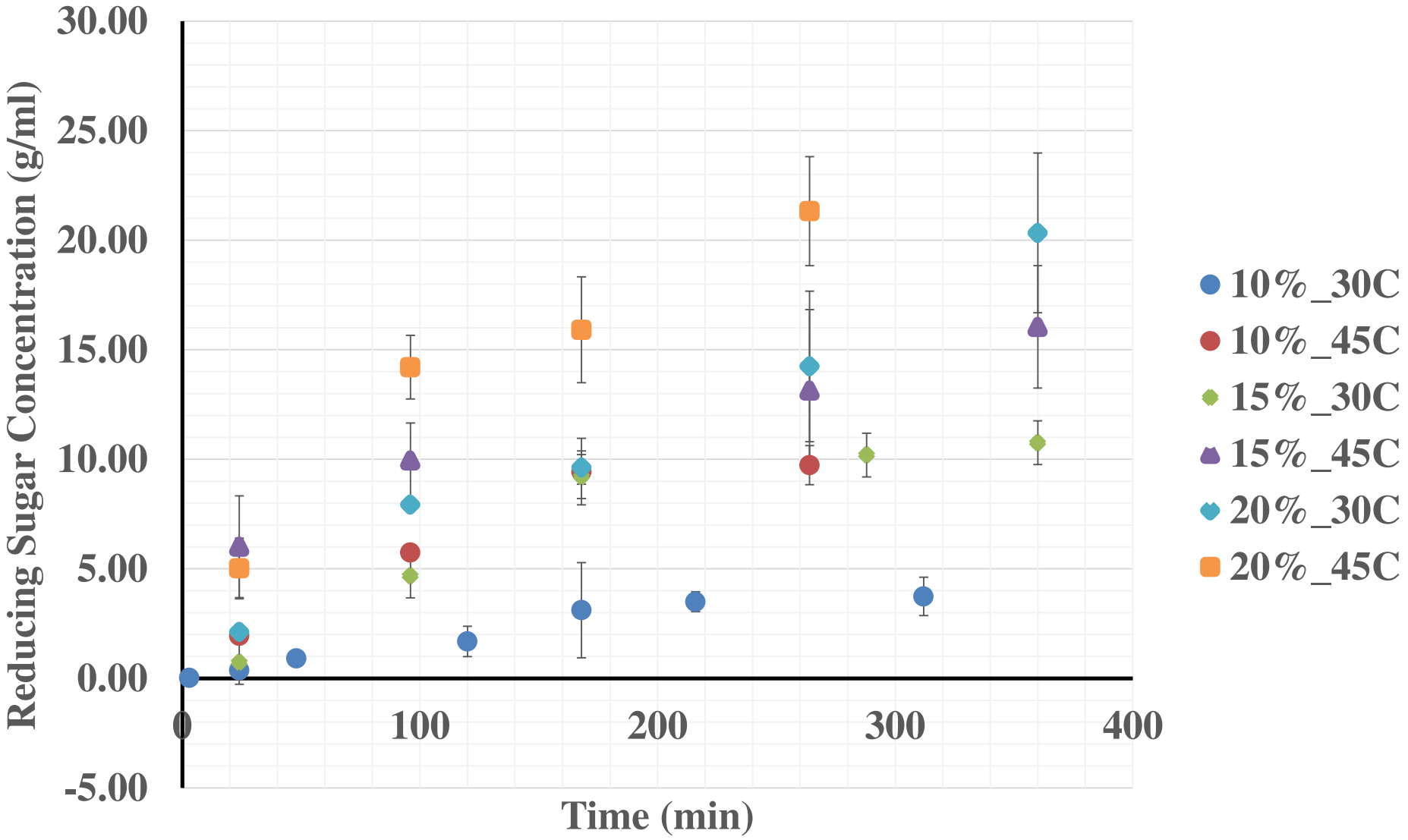
Sucrose: $[\alpha]_D = +66.5°$

D-glucose: $[\alpha]_D = +53°$ + D-fructose: $[\alpha]_D = -92°$

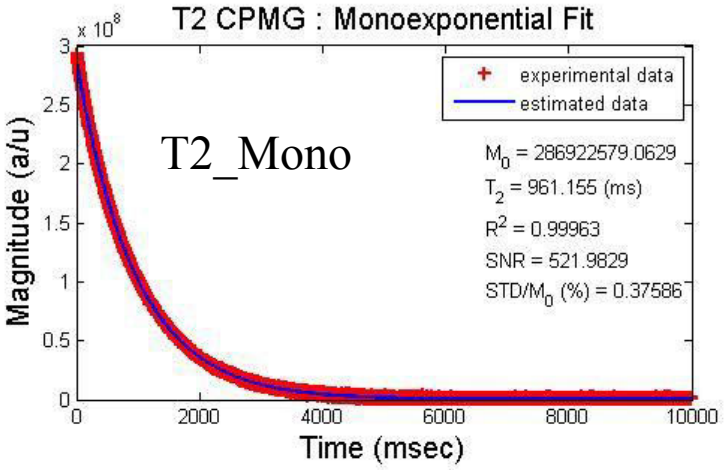
Invert Sugar

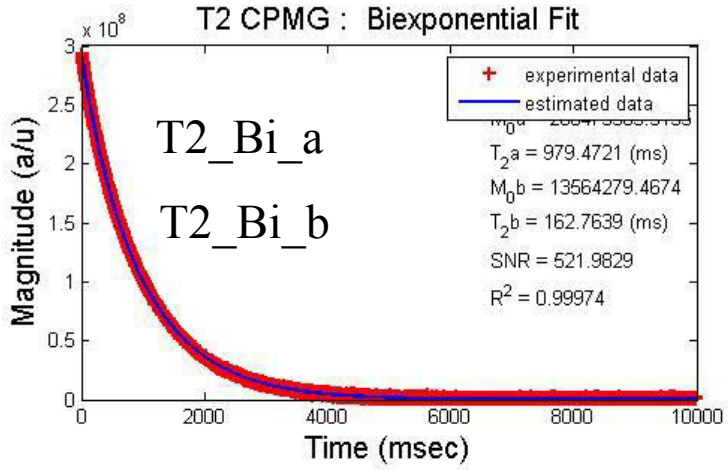
$[\alpha]_D = (+53°) - (-92°) = -39°$

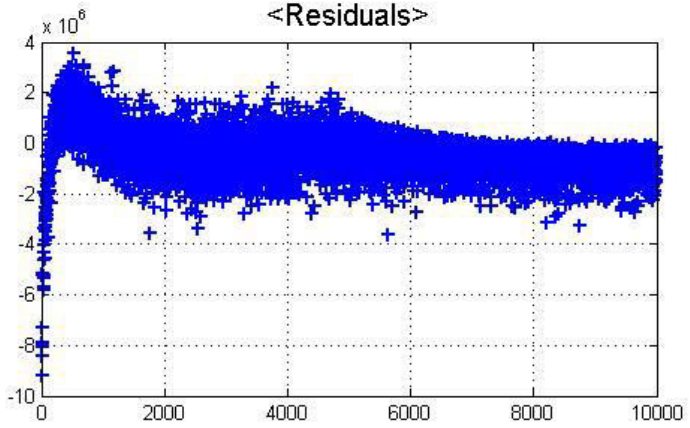

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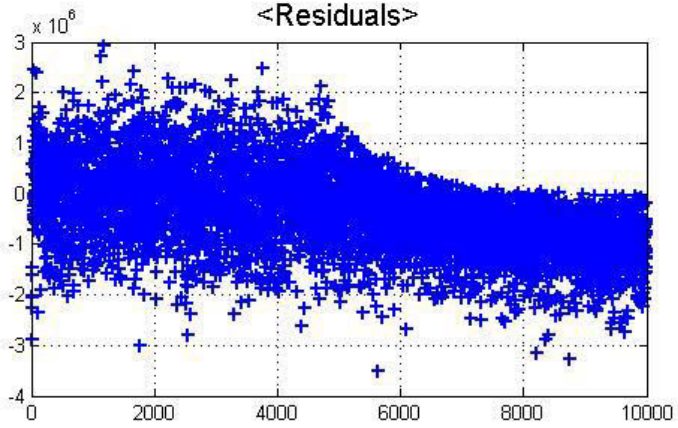


Acid Catalyzed Sucrose Hydrolysis at 10 % , 15 , 20 % sucrose concentration for 30 ^{o}C and 45 ^{o}C





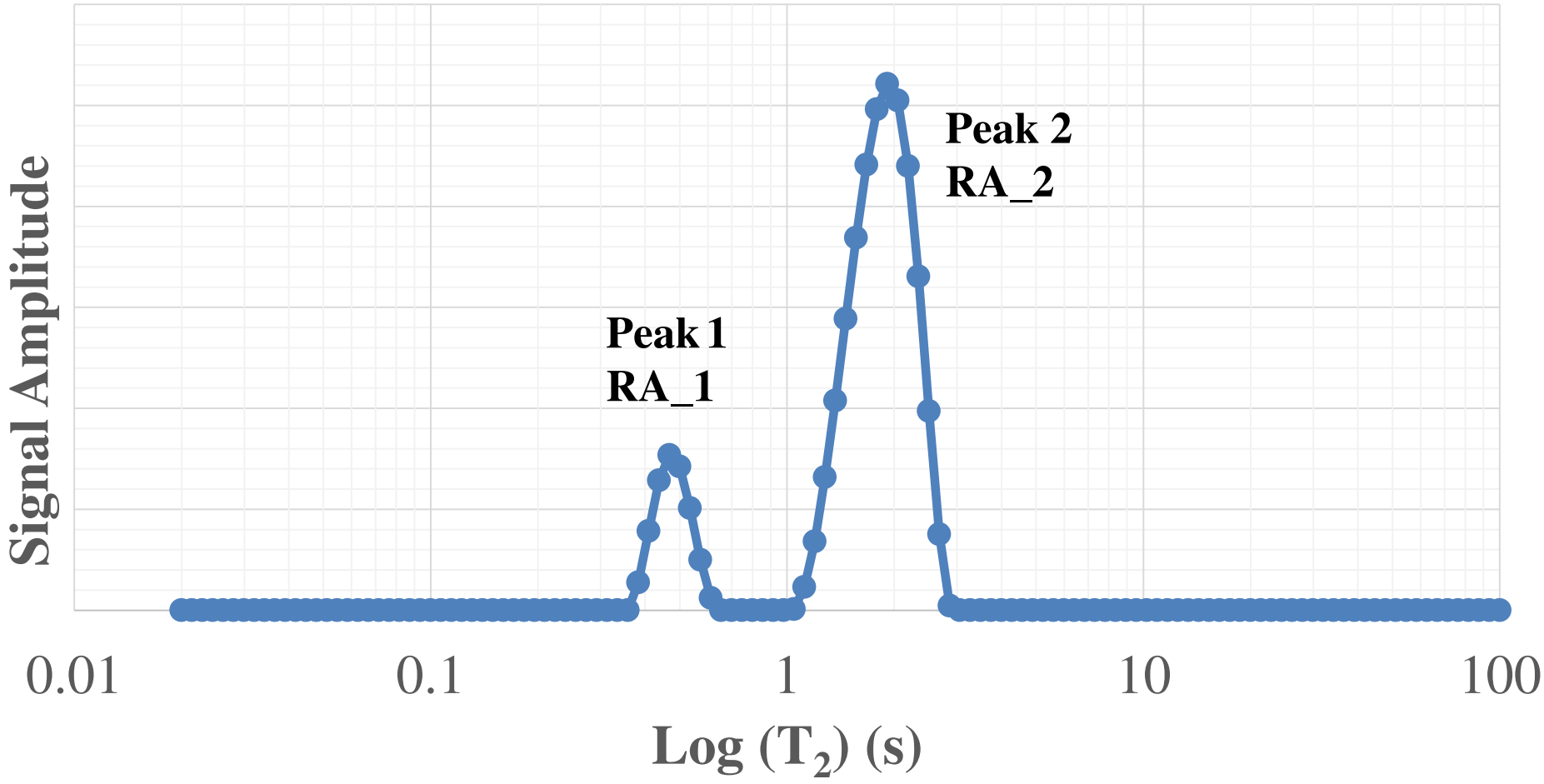




Representative T_2 CPMG Decay Curves

Mono-Exponential Fitting
Bi-Exponential Fitting

NMR T_2 Relaxation Spectrum



Monitoring Reaction by T_2 ?

10% _30 and 45 °C		10% _30 °C	10% _45 °C
T2Bi_a	-0.839		
	0.001		
T2Bi_b	0.772	0.981	0.981
	0.005	0.000	0.000
RA_1	-0.843	-0.875	-0.875
	0.001	0.010	0.010
RA_2	0.889	0.924	0.924

15% _30 and 45 °C		10% _30 °C	10% _45 °C
T2Bi_a			0.934
			0.066
T2Bi_b	0.772	0.828	0.928
	0.015	0.083	0.072
RA_1			
Peak1			0.949
			0.051

20% _30 and 45°C		20% _30 °C	20% _45 °C
T2Bi_a	0.756	0.984	0.933
	0.018	0.002	0.067
T2Bi_b	0.936	0.964	0.91
	0	0.008	0.09
RA_1			-0.929
			0.071
Peak1	0.857	0.985	
	0.003	0.002	

Conclusion

- It is definitely true that sucrose in solution is expressed as two compartments in a T_2 Relaxation spectrum.
- Longer T_2 compartment's is well correlated at different temperatures and concentrations during hydrolysis
- It is mostly associated with exchanging –OH groups in the solution.
- Fructose and Glucose –OHs could be the reason of this behavior.
- Fructose and Glucose's individual relaxation behavior should be examined.
- NMR T2 Relaxometry has the potential to be used as a reaction monitoring tool
- Wider concentration range can be used to obtain concrete results.

Questions ?