Title: Nuclear magnetic resonance for process analysis

Proposal Year: 2015-2016

Proposal Type: Renewal

Principal Investigator and other relevant personnel:

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Dr. Matt Augustine, Prof., Chemistry, University of California, Davis, phone: 530-754-7550, email: maugustine.ucd@gmail.com

Executive summary of proposed research:

During 2014-2015 we are focusing our efforts on three areas: methods for increasing the solids content in the saccarification stage of cellulose-based biofuels production; field trials of NMR to be used to analyze materials in metal containers and automating MRI based rheology measurements.

Goals and objectives: Our goal is to demonstrate the feasibility and applicability of NMR systems for process monitoring of reactions in microreactors, fermentation monitoring, environmental sample analysis, composition analysis and physical property measurement.

Specific objectives for the next year are 1) field test a handheld single-sided NMR for analysis of materials in sealed containers; 2) testing automation of in-line/on-line MRI based rheological measurements.

Budget: Our requesting budget is $15,000 to cover the expense of supplies (lab and electronic equipment), software, travel and machine shop services and 56.5% University of California overhead charges.

Background: NMR spectroscopy and imaging are some of the most advanced spectroscopic methods to characterize and quantify sample attributes from molecular structure to physical structure. NMR spectroscopy covers an extremely large range of length scales (10^{-12} to 10^{+2} m) and time scales (10^{-10} to 10^{+3} s). The main challenge in NMR is the low sensitivity and the difficulty of incorporating the equipment in a process/portable format. We are currently addressing methods to enable integration of NMR/MRI into a process. The recent developments in construction of permanent magnets, electronics and data processing have recently enabled a significant increase in the applicability and information content of NMR/MRI in industrial settings.

Research plan:

Generally nuclear magnetic resonance (NMR) has not been applied to samples in metal containers or flexible packaging with one or more metal layers. The metal used, aluminum, tends to shield the sample from the radio frequency used for excitation as well as shielding the response of the sample from detection. Since the early 90s it has been known that one can actually obtain a nuclear magnetic resonance signal from the protons in flexible packages and even soft drink cans at low magnetic field (demonstrated in McCarthy's lab work unpublished). Since the signal was weak and accurate sample measurement required long times compared to what was needed for practical inspection this approach was "tabled".

Recently in Augustine's lab new methods for rapidly measuring the signal from metal/metal lined containers have been developed. Figure 1 shows the proton spectrum from chocolate milk in a commercial aseptic package that has a thin aluminum layer. Table 1 lists two parameters that change in chocolate milk upon spoilage. It is the differences in these numbers in addition to differences in other parameters that will report on the level of spoilage and product quality in sealed metallic and non-metallic containers. A large number of tomato samples were measured in flexible metal lined bags over the last year. The spin-lattice relaxation times (T_1) changed by ~25% for spoiled samples compared to "good" samples.

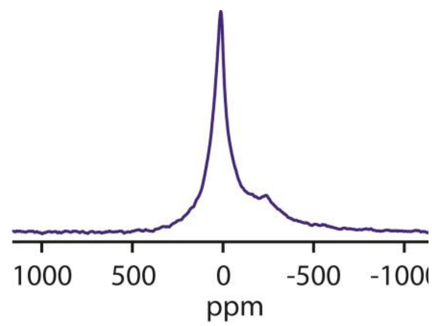

Fig. 1. One scan proton NMR spectrum of chocolate milk in metal lined aseptic bag.

Table 1. Example spoilage dependent NMR parameters in chocolate milk

Sample	T1	T2
spoiled	81 ms	32 ms
not spoiled	140 ms	60 ms

1) Field testing of the single-sided portable NMR system

The first half of last year involved developing a fundamental understanding of the magnetic field geometry offered by the handheld sensor and an appreciation for how this complicated field profile can be used to quickly and reliably deliver viscosity information to provide an estimate of tomato spoilage. The construction of an NMR based viscosity archive of pristine toted paste was initiated in late October 2014. Since that time nearly 50 totes have been analyzed and no indication of spoilage has been detected, consistent with on-site expert empirical analysis. The next phase of work over the coming year will be to broaden the archive of tested pristine paste as well as to track tested bins for evidence of spoilage that is known to develop during long term storage.

The industrial partner Cosa-Xentaur has been involved in the project throughout the past year and they have been critical to the over 1000 x improvement in sensitivity and analysis time. Their goal is to improve the sensor design and the measurement protocol to streamline the performance of the commercial device for use by non-scientists.

2) Rheology measurement automation.

We will extend the rheology measurement process to a fully automated method. The majority of our work this year will be testing additional fluids (beyond biomass) suspensions. Our software and hardware will be run on fluids and the resulting measurements compared to off-line rheological measurements to determine the accuracy and sensitivity of the automated measurement. The range of fluids will be broad from personal care products to drilling muds.

Budget Request: **Budget**:

Personnel:		
Materials and supplies		$7085
Travel		$2500
Indirect Costs:		
56.5% 07/01/15-06/30/16		$5415
	Total:	$15000

Budget Justification:

Materials and supplies:
Funds are requested for purchasing chemicals, electronics supplies, software licenses, laboratory glassware and machine shop services.

Travel:
Funds are requested to support travel of the PIs to CPAC spring meeting and partial support to present results at the IFPAC meeting in 2016 ($500).

Indirect costs at 56.5 % ($5415)

BIOGRAPHICAL SKETCH
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Education

Ph.D., Chemical Engineering, University of California at Berkeley,	1986
B.S.Ch.E, Chemical Engineering, University of Florida,	1980

Present Position

Professor and Chair. Current research projects encompass (i) optimization of industrial processes with a focus on energy efficiency; (ii) development of process control sensors (iii) measurement of fruit quality. Research sponsors include PomWonderful, Chevron, Shell, Aspect Imaging, Procter & Gamble Company.

Employment Record

Professor Departments of Food Science and Technology & Biological and Agricultural Engineering	1995-Present Davis, CA
Visiting Professor, Paramount Citrus Association and Aspect Magnet Technologies	2007 Delano, CA
Visiting Professor, Department of Food Science and Technology, Nestlé Research Center,	1996-1997 Lausanne, Switzerland
Member, Center for Process Analysis and Control, University of Washington	1995-Present Seattle, Washington
Program Leader Materials and Food Science NMR, UC Davis NMR Facility	1991-1995 Davis, CA
Associate Professor, Engineering, FST/Bio.& Ag. Engr., UC Davis	1991-1995 Davis, CA
Assistant Professor, Engineering, FST/Bio.& Ag. Engr., UC Davis	1986-1991 Davis, CA
Process Engineer, Shell Oil Company, Houston	1980-1982 Houston, TX

Honors, Awards

American Chemical Society Ag.& Fd Chemistry Division, Young Scientist Award, 1993.

Institute of Food Technologist Samuel Cate Prescott Award for Research, 1991.

National Science Foundation Presidential Young Investigator Award, 1990-1995.

Selected Manuscripts (Out of ~180)

Lavenson, D.M., Tozzi, E.J., McCarthy, M.J. and Powell, R.L. Effect of fiber length, flow rate and concentration on velocity profiles of cellulosic fiber suspensions. Acta Mechanica, in press.

Tozzi, E.J., Bacca, L.A., Hartt, W.A., McCarthy, M.J. and McCarthy, K.L., 2013. Study of Multi-lamination of a Non-Newtonian Fluid in a Split and Recombine Static Mixer using Magnetic Resonance Imaging. Chemical Engineering Science. In press.

Tozzi, E.J., Bacca, L.A., Hartt, W., McCarthy, K.L. and McCarthy, M.J. 2012. Robust processing of capillary velocimetry data via stress-rescaled velocity functions. Journal of Rheology. 56, 1499-1464.

Tozzi, E.J., Lavenson, D.M., McCarthy,M.J. and Powell, R.L. 2012. Magnetic Resonance Imaging to Measure Concentration Profiles of Solutes Diffusing in Stagnant Beds of Cellulosic Fibers. AIChE Journal 58(1):59-68.

Tozzi, E.J., McCarthy, K.L., Bacca, L.A., Hartt, W.H. and McCarthy, M.J. 2012. Quantifying Mixing using Magnetic Resonance Imaging. Journal of Visualized Experiments 59: doi: 10.3791/3493.

Lavenson, D.M., Tozzi, E.J. Karuna, N., Jeoh, T., Powell, R.L. and McCarthy, M.J. 2012. The effect of mixing on the liquefaction and saccharification of cellulosic fibers. Bioresource Technology. Online 6 Feb. 2012

Lavenson, D.M., Tozzi, E.J. McCarthy, M.J., Powell, R.L., Jeoh, T. 2011. Investigating adsorption of bovine serum albumn on cellulosic substrates using magnetic resonance imaging. Cellulose 18(6) 1543-1554.

Zhang, L. and McCarthy, M.J. 2011. Measurement and Evaluation of Tomato Maturity Using Magnetic Resonance Imaging. Postharvest Biology and Technology 67:37-43

Zhang, L, McCarthy, M.J. 2011. Black heart characterization and detection in pomegranate using NMR relaxometry and MR imaging. Postharvest Biology and Technology, 67:96-101.

Lavenson, D.M., E.J. Tozzi, M.J. McCarthy and R.L. Powell. 2011. Yield Stress of Pretreated Corn Stover Suspensions Using Magnetic Resonance Imaging. Biotechnology & Bioengineering 108(10):2312–2319.

Rakesh, V., A.K. Datta, J.H. Walton, K.L. McCarthy and M.J. McCarthy. 2011. Microwave combination heating: Coupled electromagnetics- multiphase porous media modeling and MRI experimentation. AICHE J. 23 MAY 2011, DOI: 10.1002/aic.12659

Roberts, K.M., D.M. Lavenson, E.J. Tozzi, M.J. McCarthy and T. Jeoh. 2011. The effects of water interactions in cellulose suspensions on mass transfer and saccharification efficiency at high solids loadings. Cellulose. 18(3):759-773.

Garcia, S, J.H. Walton, B. Armstrong, S. Han and M.J. McCarthy. 2010. L-band Overhauser dynamic nuclear polarization. Journal of Magnetic Resonance. 203(1):138-143.

Rakesh, V., Y. Seo, A.K. Datta, K.L. McCarthy, and M.J. McCarthy. 2010. Heat Transfer during Microwave Combination Heating: Computational Modeling and MRI Experiments. AIChE Journal. 56(9):2468-2478.