Practical Applications of Compact, Cryogen-Free High-Resolution 60 MHz Permanent Magnet NMR Systems for Reaction Monitoring and Online/At-Line Process Control Observing ^{1}H, ^{19}F, and ^{31}P

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Aspect 60 MHz NMR System

Abstract

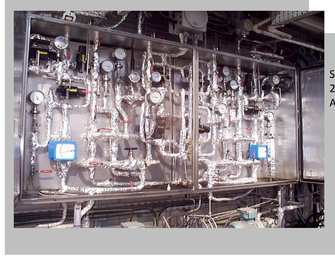
For the past two decades high resolution ^{1}H NMR at 60 MHz has been utilized to monitor the chemical physical properties of refinery and petrochemical feedstreams and products[1]. These approaches involve the use of partial least squares regression modelling to correlate NMR spectral variability with ASTM and other official test methods, allowing the NMR to predict results of physical property tests or GC analysis. The analysis is performed in a stop flow environment where solenoid valves are closed at the beginning of the NMR experiment. This approach allows up to 5 or 6 different sample streams to be sent to the sample in order to maximize the impact of the instrument. The current work with these permanent magnet NMR systems is to utilize them as chemistry detectors for bench-top reaction monitoring, mixing monitoring, dilution monitoring, or conversion monitoring. In the past use of NMR for these applications has been limited by the need to bring the "reaction" to the typical "superconducting" NMR lab. A compact high resolution NMR system will be described that can be situated on the bench-top or in the fume hood to be used as a continuous or stop-flow detector and/or an "in-situ" reaction monitoring system. The system uses a unique 1.4 Tesla permanent magnet that can accommodate sample diameters of 3-10 mm with half-height resolution approaching 1-3 Hz (depending on the sample size) and excellent single pulse sensitivity. Reaction monitoring can be performed using a simple flow cell analyzing total system volumes of 2 to 5 mL depending on the length and diameter of the transfer tubing. Further, detection limits of analytes in the 200+ ppm range are possible without the use of typical deuterated NMR solvents. Analysis times of 5 to 20 seconds are also possible at flow rates of 1 to 20+ ml/minute. Reaction monitoring directly in standard 5-10 mm NMR tubes using conventional (non-deuterated) reactants, solvents and analytes will also be described. Examples of ^{1}H, ^{19}F and ^{31}P analyses will be described.

1. "*Process NMR Spectroscopy: Technology and On-line Applications*" John C. Edwards, and Paul J. Giammatteo, in **Process Analytical Technology: Spectroscopic Tools and Implementation Strategies for the Chemical and Pharmaceutical Industries, 2nd Ed.,** Editor Katherine Bakeev, Blackwell-Wiley, 2010

1st Generation NMR Analyzer
Invensys –Foxboro - 1998-2003

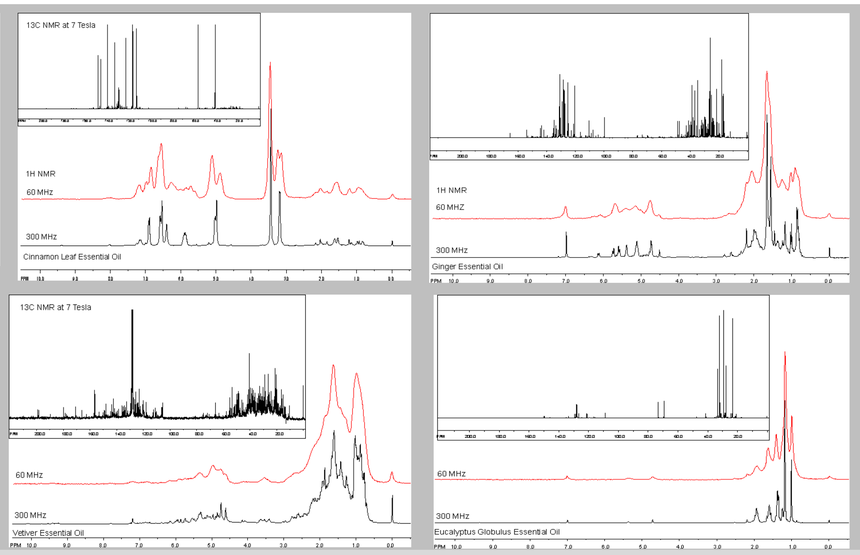
2nd Generation NMR Analyzer
Qualion Ltd. 2003-2011

3rd Generation NMR Analyzer
Modcon-Xentaur-Aspect AI

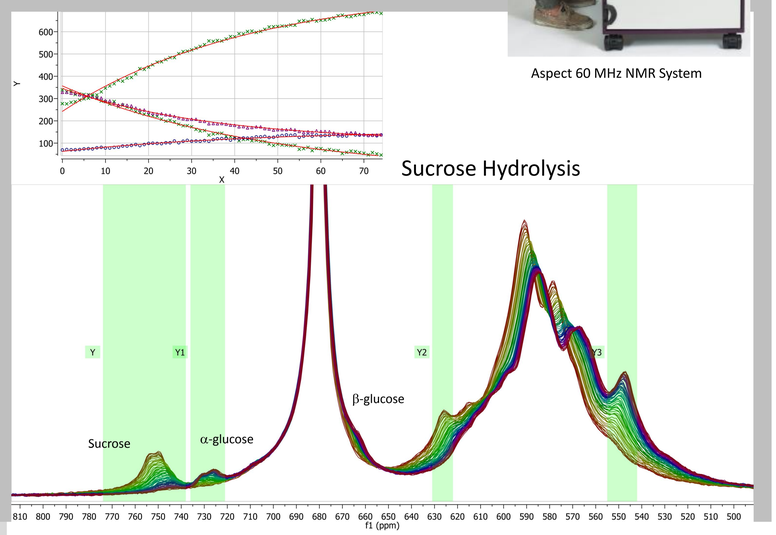


Sample system providing
2 conditioned streams to NMR
Analyzer

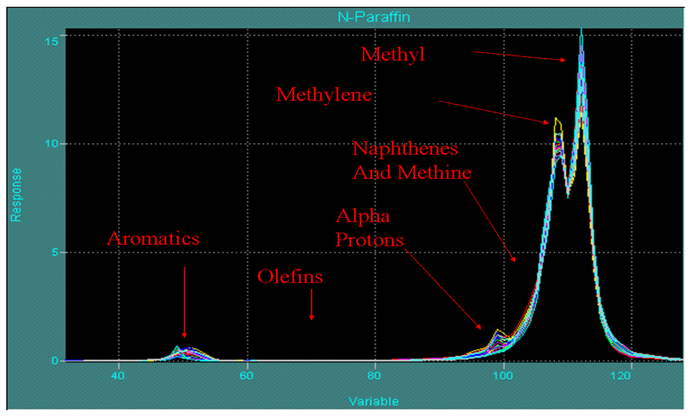
Typical NMR Analyzer
Environment
Shelter House at Base of
Vaccuum Tower



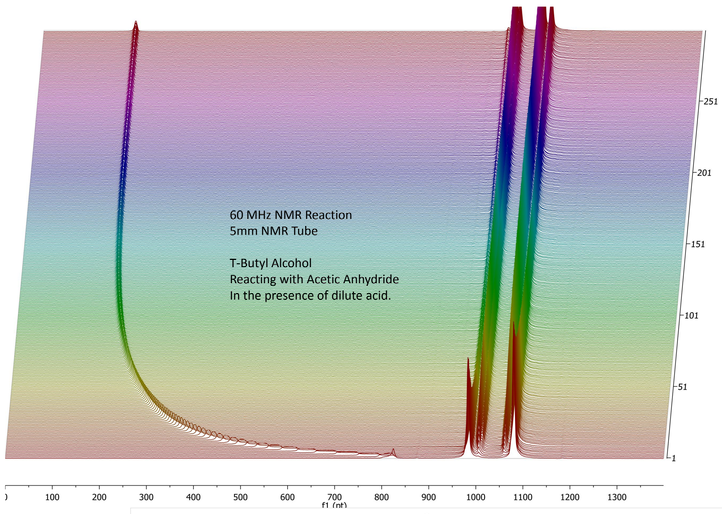
Examples of the expected resolution obtained on various essential oils at 60 MHz

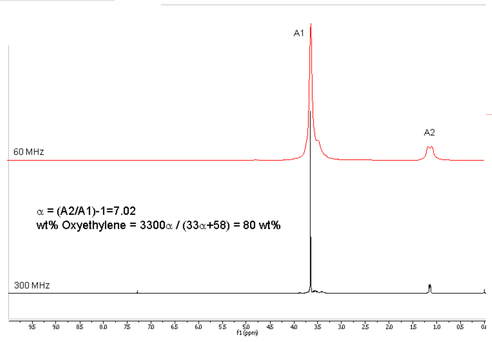


Example Application: Steam Cracking Optimization Installed at BASF, Ludwigshaven 2000
Cracker Facility Capacity: 600,000 Tonnes per Year
Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO Optimization
NMR Analysis: 3-4 Minute Cycle (Single Stream)
NMR PLS Outputs: Naphtha – Detailed Hydrocarbon PONA Analysis, Density
C4-C10 normal-paraffin, iso-paraffin, aromatics, naphthenes

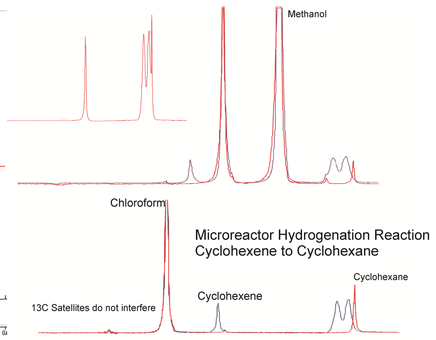


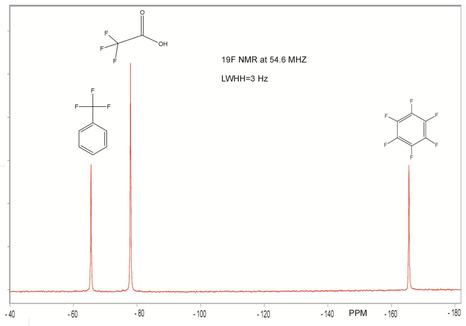
Spectral Variability Observed in Naphtha Samples

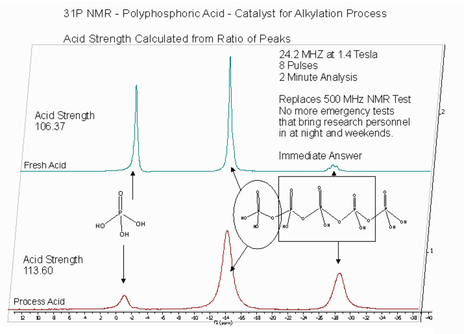


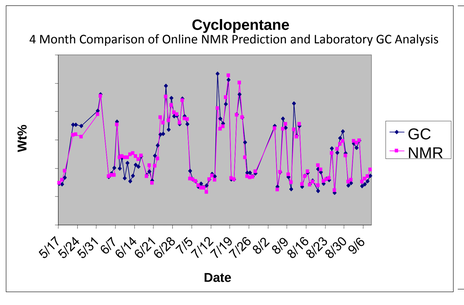


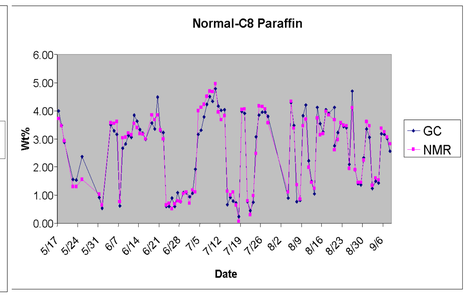
Poloxamer - Oxyethylene and Oxypropylene Content - USP/NF Method

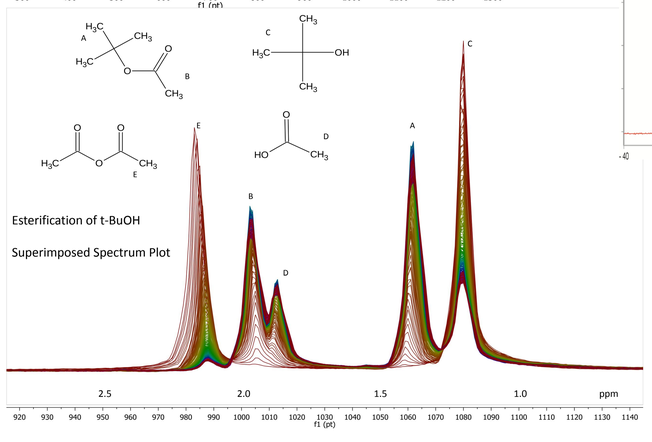


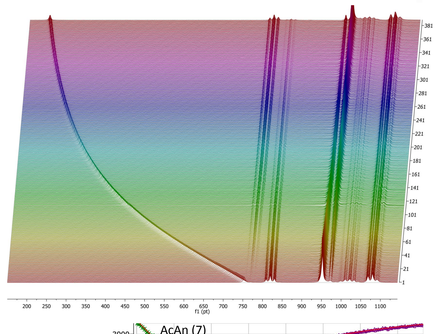




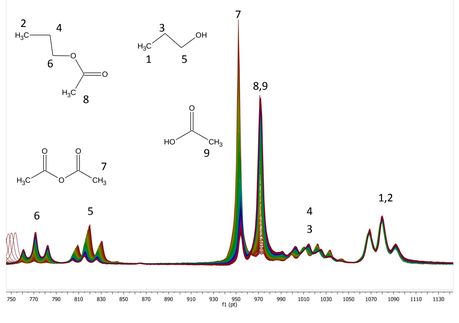


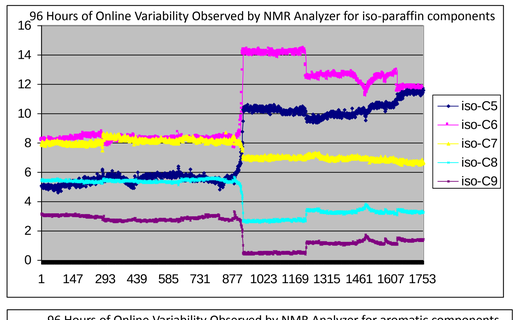


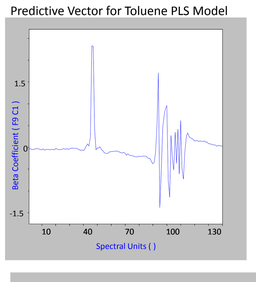


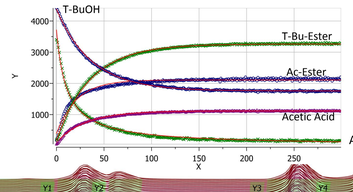


1-Propanol Esterification with Acetic Anhydride
Pure Solution – No Solvent – No Acid Catalyst
8 Hour Reaction Profile



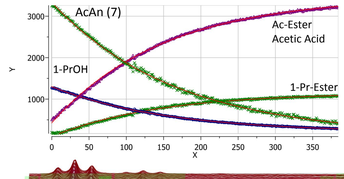


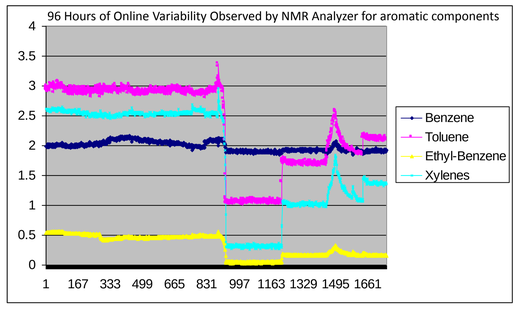


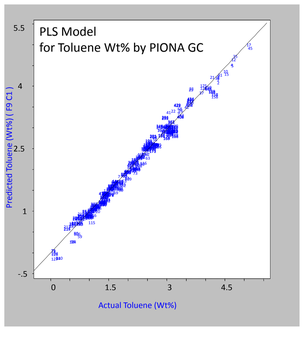


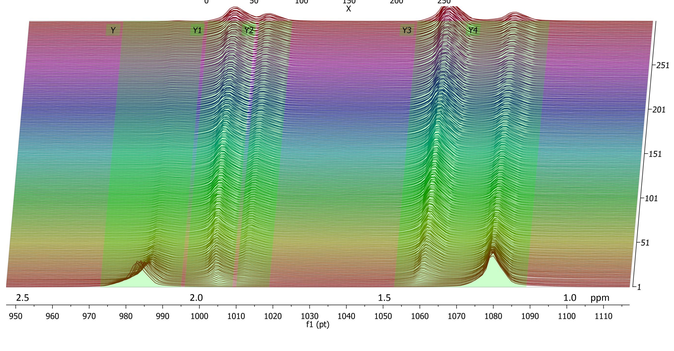
Esterification of t-BuOH

Integral Graph
And Integration Plot









Esterification of 1-Propanol by Acetic Anhydride
Integral Plots for Reaction Profile