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Process NMR: A Complete Solution for the Biofuel Industry

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Abstract

The rapid global development of biofuel technologies has created a demand for new advanced analytical methodology. The diversity of biofuel feedstock materials poses a significant challenge for rapid, robust analysis by traditional analytical techniques. Nuclear Magnetic Resonance (NMR) is emerging as a complete solution for meeting the new analytical challenges of screening genetically modified seeds, new strains of algae, pretreatment of biomass feedstocks and for final quality verification of biofuels. The use of NMR relaxation time methods in combination with advanced data processing yields high correlations with key properties of feedstocks, biofuels and important intermediate process parameters. We introduce the state-of-the-art NMR solutions for research and industrial applications available today which provide fast reliable analysis for the biofuel industry.

Key Words: Algae, biodiesel, biofuel, biomass, cellulosic ethanol, feedstock, NMR, TD-NMR

Introduction

Since being the subject of the Nobel Prize for Physics in 1952, NMR has expanded to become one of the most advanced methods for detailed research and development of liquids and solids. High-resolution NMR systems have become the primary method for structural analysis of proteins and other chemical analyses. High magnetic field systems are now being produced to measure at 1GHz with resolution to observe subtle differences in complex materials. In the medical field, NMR continues to evolve to provide doctors and patients with some of the most effective non-invasive techniques for imaging tissues in the human body.

Another fast growing segment for NMR technology development and application is the utilization of industrially hardened Time-Domain NMR (TD-NMR). The first markets for TD-NMR included food products with initial work based Solid Fat Index (SFI) and Solid Fat Content (SFC), baked goods and moisture in grains. Further advances in system electronics capability, computing speed and data analysis methods have resulted in new opportunities with TD-NMR in polymers, mining, agriculture and fuel production. Current TD-NMR International standards include SFI methods (ISO-8292 and AOCS cd 16b-93), oilseeds (ISO-10565 and 10632) as well as in aviation fuel analysis (ASTM-7171). Modern TD-NMR systems with significant capability and user flexibility have enabled numerous research and production organizations to cost effectively improve analytical characterization. Borealis AG

has been using on-line NMR technology since 1995 for controlling and monitoring tacticity parameters such as xylene solubles (XS) and total ethylene content (C2) in its polypropylene processes. The instances where NMR has picked up and/or confirmed process disturbances have been numerous, thus avoiding plant shutdowns on a large scale and improving product consistency on a smaller scale (Garner 2005). Since the introduction of TD-NMR to the polypropylene market in the early 1990s, the industrial acceptance has rapidly grown with more than 90% of polypropylene producers in North America and Europe adopting this method for research and production purposes.

Based on the success of TD-NMR techniques noted above, innovative leaders in the emerging biofuel industry have also looked to TD-NMR with urgency to meet the analytical needs of new research efforts and for optimization of new biofuels production processes.

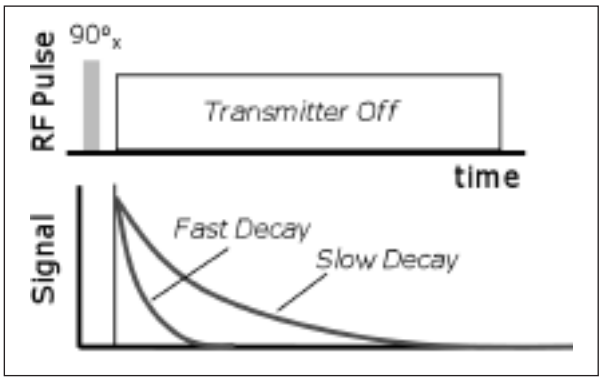
Nuclear Magnetic Resonance

The basis of the NMR technology is the interaction of a nuclear spin with its electro-magnetic environment. Although the hydrogen nucleus is the most commonly used, and the one providing the highest sensitivity, several other nuclei can be detected by NMR.

In the presence of a static magnetic field, B_o, the resonance frequency of the nuclear spin is related to the magnetic field strength through the Larmor equation, $\nu = (\gamma/2\pi)\, B_o$, where γ is the magnetogyric ratio of the nuclei under study. For example, protons in a field of 0.5 Tesla have a resonance frequency of ν = 21 MHz. Typical frequencies of operation are in the MHz range and therefore NMR is a radio-frequency (RF) technique. The electromagnetic emissions are non-ionizing and consequently NMR and MRI are safely used in humans.

After the application of an RF pulse, a non-equilibrium state is achieved in the spin system of the analyzed specimen. The magnetization then relaxes back to equilibrium, precessing under the action of the magnetic field. This induces a measurable voltage in the receiver probe. The induced voltage is the experimental NMR signal termed free induction decay, or FID. The time domain signal may be Fourier transformed to produce a spectrum. The investigation of frequency shift components during the signal decay leads to the field of NMR spectroscopy, while the analysis of signal lifetime correlation to materials properties is known as NMR relaxometry or TD-NMR.

The decay of transverse magnetization in a FID is governed by a time constant, T_2^*, $M_{xy} = M_o \exp(-t/T_2^*)$. This parameter incorporates magnetic field inhomogeneity effects, which lead to dephasing of transverse magnetization and consequent signal decay.



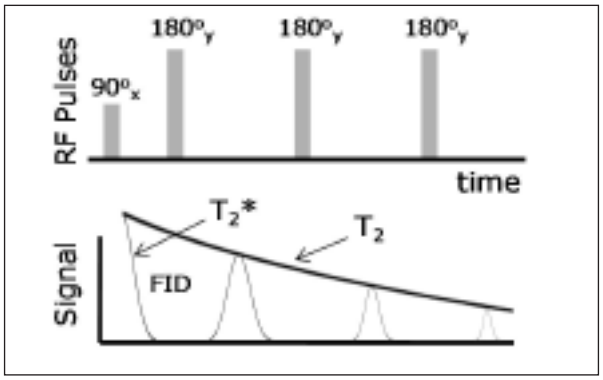
Excitation and response of the magnetization after a single RF pulse. The 90°pulse rotates the magnetization to the plane perpendicular to B_0. The signal decays with a relaxation time T_2^*, the life-time of the FID.

Internal magnetic interactions are characterized by the spin-spin relaxation, T_2. This process involves interactions between neighboring spins. The T_2 and T_2^* time constants are related through inhomogeneity in the static magnetic field, ΔB_0 , by, $1/T_2^* = 1/T_2 + \gamma \Delta B_0/2$.

The T_2 time constant may be assessed with a measurement known as spin-echo, invented by Erwin Hahn (Hahn 1950). A 90° excitation pulse (magnetization tilted to the transverse plane) followed by one or more 180° pulses produce spin echoes. The decay of the echo amplitudes is given by the exponential time constant T_2.

The net magnetization recovers after excitation to its equilibrium value according to $M_z = M_o [1-\exp(-t/T_1)]$. Spin lattice relaxation involves interaction and energy exchange between the spins of the sample and their surroundings. The T_1 time constant characterizes the recovery of magnetization in the static field direction.

For liquid samples in a highly homogeneous magnetic field, the T_1 and T_2 time constants may be seconds. For systems which do not reveal liquid like molecular motion, such as rigid solids or samples with confined water or fluid content and/or highly ordered molecular scale structure, the T_2 relaxation time can be reduced to msec or µsec. The relaxation time constants, through sensitivities to different time scales of motion, report on the dynamics of the system under study.



The Carr-Purcell echo pulse sequence for T_2 measurements. The initial 90° pulse rotates the magnetization onto the plane perpendicular to B_0, and the following sequence of 180° pulses refocuses the static field inhomogeneities while the signal is acquired.

Originally of interest to study the magnetic properties of atomic nuclei, it was soon recognized that the magnetic fields at the site of the nucleus in a molecule are modified by the magnetic fields induced from the motion of the bonding electrons. This field shift bears valuable chemical and structural information. Thus an NMR signal is observed for a particular nucleus in a molecule, which is a fingerprint of the chemical structure. Additionally, the signal lifetime is driven by molecular mobility and various structural characteristics associated with pathways for the spin system to exchange energy.

Molecules in liquids and soft materials are readily observable by NMR because the through-space magnetic interaction is weakened by molecular motion. This has allowed for the widely adopted chemical NMR and clinical MRI methods. On the other hand, fast signal decays resulting from stronger magnetic interactions are characteristic in rigid and semi-rigid materials. Special TD-NMR techniques, such as the spin-echo method described above, are then used to evaluate materials, even in the presence of inhomogeneous static magnetic fields.

Spectroscopic expansions of the signal are observed using high strength homogenous field instruments requiring cryo-cooling. Therefore dedicated facilities are necessary for spectroscopic NMR and clinical MRI applications. On the other hand, material analysis with TD-NMR probes using permanent magnets and robust hardware configurations require minimal maintenance and limited bench space. Commercial self-calibrating TD-NMR instruments (www.progression-systems.com) are utilized for on-line testing and for laboratory analysis.

Biofuel Characterization

The quality control of biofuels is critical to the success of its production and the ultimate energy efficiency achieved. Various analytical techniques are emerging for the characterization of biofuels. Gas Chromatography (GC), High Precision Liquid Chromatography (HPLC) (Monteiro 2008), Infrared (IR) (ASTM D7371-07) and thermogravimetric analysis (TGA) are methods aiding biofuel examination. As an alternative and complementary to optical methods, NMR detects and characterizes elements in the bulk of the sample. NMR measurements are attained non-invasively and therefore samples can be consecutively analyzed by other correlating reference methods. As an example, biodiesel content in diesel fuels is analyzed by IR, using NMR as the primary method to measure biodiesel content (Asakuma 2007, Tan 2001). TD-NMR has demonstrated to be effective at determining the quality of oilseeds with modified fatty acid profiles (Prestes 2007).

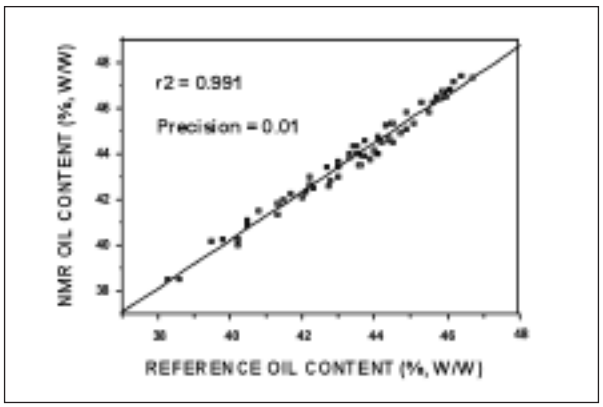
NMR has been used extensively with vegetable oil feeds, reaction intermediates, and final products of the biodiesel transesterification process (Carneiro 2006, Ramadan 2001). Novel NMR methods reportedly determine free fatty acid content in vegetable oils, animal fats, in addition to biofuels (Chuck 2009). Furthermore, NMR data analysis by Partial Least Squares and Principal Components Regression models is suitable for the prediction of biodiesel and oil concentration in mineral diesel (Monteiro 2009, Monteiro 2009B).

Rapid determination of lipid content in microalgal cells is critical to optimize the process of fermentation to minimize costs of alga-based biofuel production (Gao 2008). TD-NMR offers the capability of quantifying lipid content during algal fermentation.

NMR Solutions for Biofuels

Due to the flexibility of NMR spectroscopy noted above and the emerging biofuel industry analytical needs, there has been an explosion of newly published NMR results in the past few years. NMR developments have been made in the field of research, quality assurance and process optimization.

The utilization of TD-NMR for research and development in the biofuels industry has included several areas of study. The rapid non-destructive analysis of oilseeds provides scientists and breeders with reliable feedback for the oil content of the seeds under examination. The graph below shows NMR results for oil content in seeds covering a wide range of oil levels.

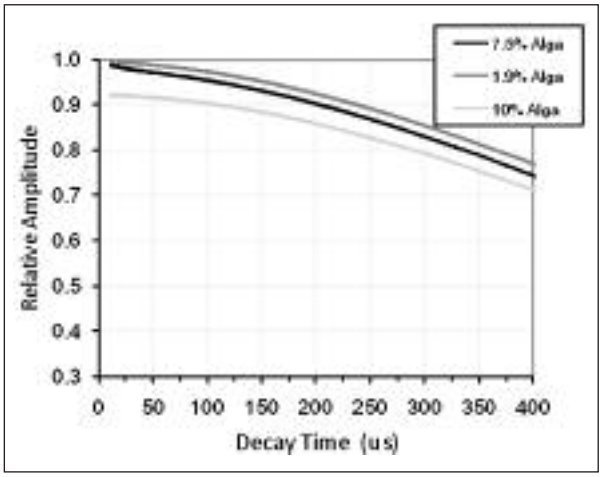


NMR results for oil content in rapeseeds.

In addition to having good accuracy over a full range of oil content (SEC 0.3%), NMR also demonstrates excellent repeatability with mid-range precision of 0.01 %.

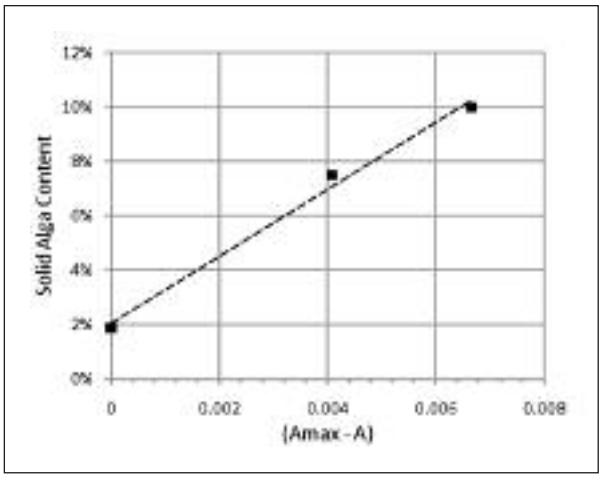
Oil seed analysis for research purposes can be performed on whole seeds or pre-ground seeds. High throughput seeds analysis for multiple properties including oil quality of intact seeds by its fatty composition, cetane number, iodine value and kinematic viscosity have been performed. Up to 1000 samples per hour were measured with a correlation coefficient $r > 0.9$ for the above properties (Prestes 2007).

Progression, Inc. is developing a novel NMR technique to measure the concentration of solid alga in water. The signal amplitude and lifetime are calculated and compared to the relative solid content determined by gravimetric methods. A linear trend is observed in the NMR predictions. The data below was collected using a Progression MagStation II™ NMR system for analysis of spirulina algae.



NMR signal decay time for three solid content levels of algae

The signal amplitude is presented against the relative solid content. A linear trend is observed in the NMR predictions for solid alga to water content.



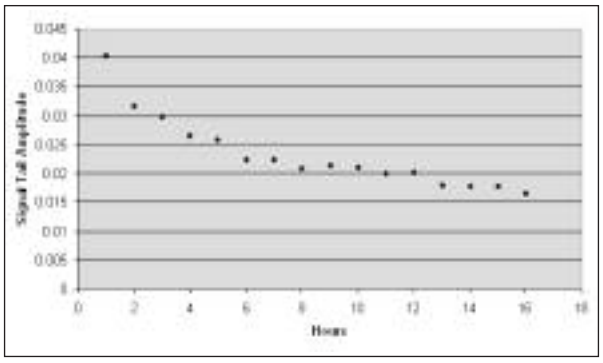
Solid algae content correlation to NMR signal amplitude

In addition to the use of NMR for solids content, other findings have shown NMR to be very well suited for lipid analysis in algae. NMR methods

have been reported to provide better agreement (R^2=0.9973) with the measured values from lipid extraction experiments than the Near-infrared staining method (R^2=0.9067). (Gao 2008)

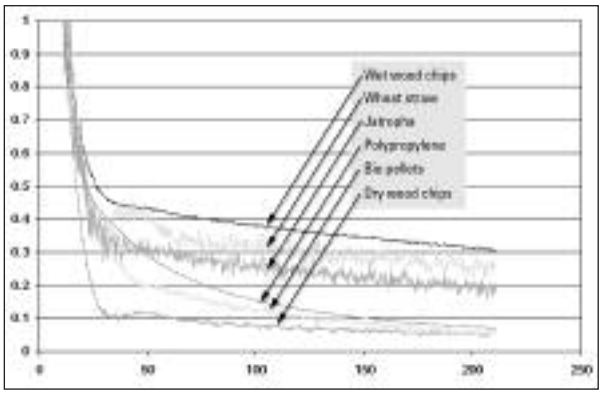
Feasibility studies of biomass materials for cellulosic ethanol have also used NMR to classify feedstock materials and investigate water migration into the plant cell walls. In these materials, water is typically found in sites within a plant matrix. Chemically bound water is found in the cellulose matrix, bound water in the plant fibers, and free water in between the fibers and in the lumens. NMR is able to measure the water located in each of these forms. Further data analysis leads to the ability to track the change in water as it migrates from one form to another.

The graph shown below tracks the NMR signal change over time as moisture is absorbed into cell walls of a corn cob. The contribution of the free water to the total hydrogen signal decreases as the water is absorbed into the cell walls of the biomass. Similar studies have been performed using wheat grass, corn stover and other biomass materials.



Water absorption in the cell walls of corn cob

The water migration in various biomass feedstocks is an important parameter as it impacts the ability for enzymatic hydrolosis to take place. Crystallinity of plant cell wall material is also a determining factor. NMR has been successfully used for many years to monitor the crystallinity of polymer materials such as wax, polystyrene, polyethylene, polypropylene and others. Similar NMR techniques can be applied to plants to determine the crystallinity of cellulose. The graph below shows the similarity between the free induction decay curves for man made polymer materials and biomass materials.

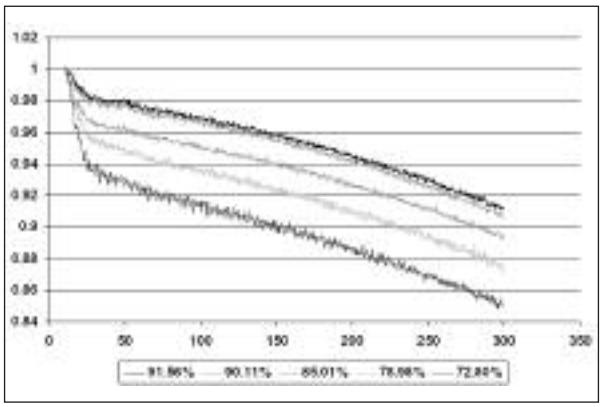


NMR signal decays for various semi-crystalline materials

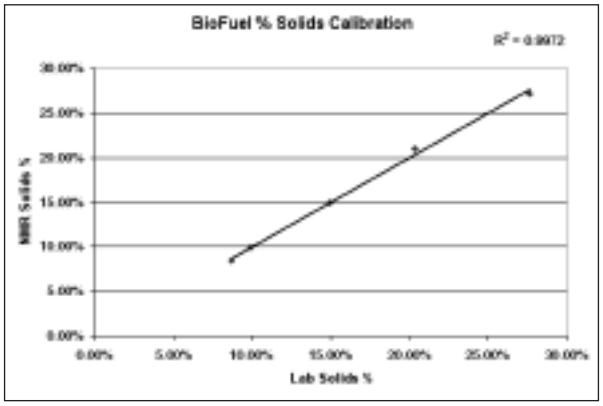
Further studies have shown that the hydration of cellulose results in an increase of crystallinity, indicating the amorphous components become more ordered with the addition of water. (Park 2009)

In recent, years the trend of NMR instrumentation has continued to move from lab-based analysis towards process control and process optimization. As biofuels production facilities scale up from pilot plant stage to commercial plant scale, periodic lab based analysis no longer meets the challenges of a full-scale plant. Only on-line NMR instrumentation with real-time process feedback of key properties can satisfy the need for commercial production facilities. Although on-line process NMR has been used commercially for years in the food, mining and petrochemical industry with success, it is only within the past year that such progress has made it to the growing biofuels industry. One such example is with respect to the analysis of undisolved solids content in cellulosic ethanol production. NREL has reported that operating with higher-solids concentrations in the biorefining process is one important factor in reducing ethanol costs. The ability to reduce water as part of the pretreatment step also reduces equipment and energy costs for the process. Process NMR has demonstrated excellent capability for the on-line process analysis of solids content in biorefining. The data below show the NMR signals and calibration results for wheat straw of various solid/water levels. Other tests have demonstrated similar results for other biomass

feedstocks including corn stover, corn cobs, woodchips and switch grass.



NMR signal decay for wheat straw slurries of various moisture levels



Correlation of NMR signal amplitude to biofuel's solid contents.

Conclusion

NMR provides automated high-throughput bulk property analysis, leaving specimens intact. Measurements are performed without direct exposure to the sample and with minimal sample preparation.

The utilization of TD-NMR for biofuels includes a full range of application solutions such as research and development efforts, quality assurance testing, on-line continuous process optimization and continuous real-time quality control. The NMR results presented demonstrate the flexibility, accuracy and reliability required for the analytical challenges faced in the biofuels industry. Continued efforts toward application development, process scale-up and commercialization will result in more wide-spread use of TD-NMR as an international standard for the biofuels industry.

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