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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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 feedstocks and products. These approaches involve the use of partial least squares regression modelling to correlate NMR spectral variability with ASTM and/or 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 solvent volumes are closed at the beginning of the NMR experiment. This approach allows up to 3 or 4 different sample streams to be sent to the sample in order to minimize 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 furnace head to be used as a transmission or stop-flow detector and/or an "in situ" reaction monitoring system. The system uses a unique 4.1 Tesla permanent magnet that can accommodate sample diameters of $10$ mm with half-height resolution approaching $1$ Hz (depending on the sample size) and excellent single pulse sensitivity. Reaction monitoring can be performed using a simple flow cell analyzing system volumes of 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 possible at flow rates of 15 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.