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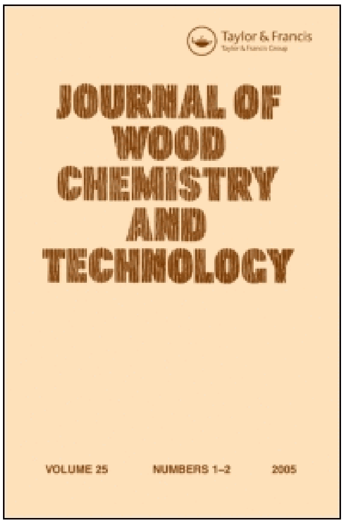

Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Draheim, E. J. and Ragauskas, A. J.(1997) 'NMR Studies II. Investigation of Process Analytical NMR Techniques for the Pulp and Paper Industry[1]', Journal of Wood Chemistry and Technology, 17: 3, 287 — 296
To link to this Article: DOI: 10.1080/02773819708003132
URL: http://dx.doi.org/10.1080/02773819708003132

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 17(3), 287-296 (1997)

NMR STUDIES PART 2:
INVESTIGATION OF PROCESS ANALYTICAL NMR TECHNIQUES FOR THE PULP AND PAPER INDUSTRY[1]

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ABSTRACT

The application of a low-field NMR spectrometer, specifically designed for industrial applications, was explored as a means of characterizing the physical properties of kraft black liquors. A variety of proton NMR parameters were determined for black liquor samples, including relative signal intensities and T_2 measurements. These values were correlated against the % solids and viscosity values of these samples. Research studies demonstrated that it was readily feasible to measure % solids for a variety of kraft black liquor samples by determining the proton NMR signal intensity for each of these samples.

INTRODUCTION

Changes in industrial environmental compliance issues and the growing demand by consumers for the production of high quality products with minimal environmental impact have brought profound changes to many industrial manufacturing processes.[2] In response to these needs, a renewed emphasis has developed for process analytical chemistry (PAC) techniques. PAC equipment such as XRF, GC/MS, FT-IR, Near-IR, and UV/Vis has been introduced into a variety of industrial settings.[3] In the pulp and paper industry, the use of brightness sensors for pulp bleaching operations is a commonly accepted practice,[4] and recently, Varma and Krishnagopalan have examined the use of at-line HPLC-UV/Vis on black liquor as a viable method for improving the kraft pulping process.[5] Birkett and Gambino have examined the use of NIR to estimate pulp kappa number,[6] and Woitovich et al. have shown that semichemical pulp yields can be determined employing this spectroscopic method.[7]

Notably absent from this list of analytical techniques is the use of NMR. Advanced NMR techniques hold several distinct advantages for PAC methods, including the possibility of on-line, real-time analysis of complex mixtures with little, if any, sample preparation required. It is interesting to note that industrial NMR PAC applications were identified as early as 1956, but the technical challenges of maintaining a NMR spectrometer in an industrial setting were found to be too challenging.[8]

Recent advances in magnetic design, electronics, and computer software have dramatically enhanced the potential use for real-time NMR process control in an industrial setting. This paper examines the use of a PAC NMR spectrometer specifically manufactured for industrial applications. Although numerous possibilities exist for the industrial use of NMR in the production of paper-related materials, our initial studies were directed toward evaluating the physical properties of black liquor. Efficient processing and combustion of black liquor require characterization of several physical parameters, including % solids, viscosity, and heating value. Despite substantial research into the development of on-line sensors for characterizing black liquor, few reliable methods are available. The most commonly applied methods employ refractive index,[9] liquor density,[10] or total organic carbon content measurements,[11] all of which must be performed off-line.

A review of applied NMR studies indicates that low-field NMR spectrometers have been applied to characterize numerous properties relevant to manufacturing processes. Early studies by Shaw and Elsken in 1953 demonstrated the application of NMR to measure water content in food products.[12] Ladner and Stacey applied these methods to flowing aqueous coal slurries[13] and developed linear relationships that correlated the signal intensity of the water signal to moisture content. Viscosity measurements of petroleum oils and tar sand bituminous have been accomplished by measuring T_2 values and correlating these to calibration curves derived by measuring T_2 values for a series of standard samples.[14] In summary, at the onset of these studies, literature results suggested that NMR methods could provide a new means of measuring several important black liquor parameters that were relevant to industrial applications. This paper summarizes some of our initial investigations into this field.

RESULTS AND DISCUSSION

Although NMR analysis of lignin fragments recovered from pulping liquors is frequently performed, to date, there have been few published articles characterizing crude pulping liquors. Representative ^{1}H NMR spectral data acquired with a high-field and PAC NMR spectrometer operating at 400 and 60 MHz, respectively, are shown in Figure 1.

The chemical shifts centered at δ1.5, 3.2, 4.5, 6.4, and 8.3 ppm can be readily assigned to aliphatic groups, carbohydrate/methoxy signals, water and aromatic components, respectively. To investigate the process control value of these data, we correlated the magnitude of the proton FID signal acquired from the low-field spectrometer to the percent solids for pulping liquor I at several dilution factors. The results of these studies are summarized in Figure 2.

These data demonstrate a near linear relationship between the magnitude of the proton NMR FID signal and the percent solids of the pulping liquor. Of

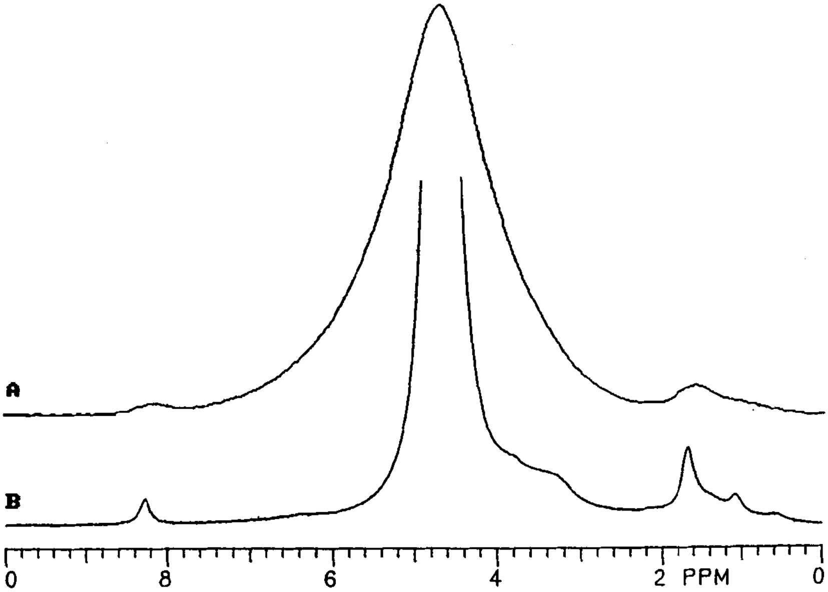

Figure 1. ^{1}H NMR spectral data acquired from black liquor sample I with (A) PAC 60 Mhz NMR spectrometer and (B) 400 Mhz NMR spectrometer.

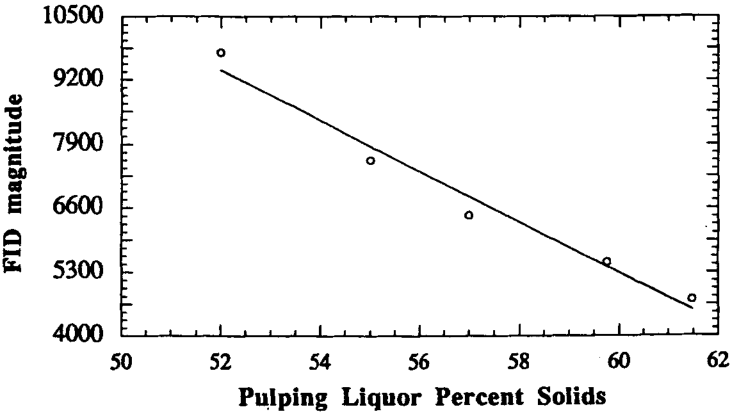

Figure 2. Percent solids versus the magnitude of the ^{1}H NMR FID signal for black liquor sample I at five different dilution factors.

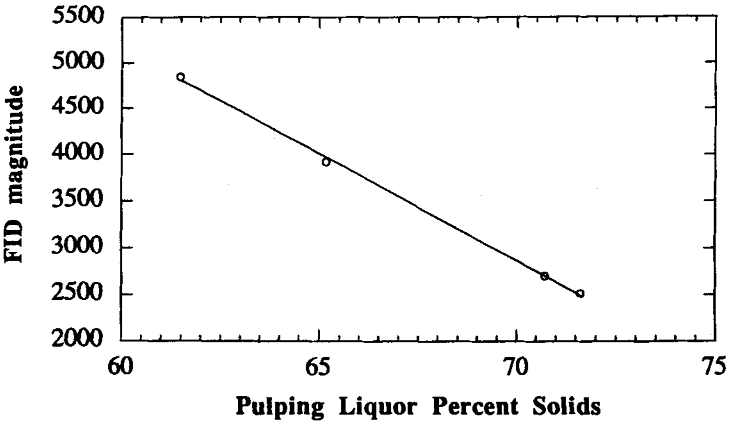

Figure 3. Percent solids versus the magnitude of the ^1H NMR FID signal for four different black liquor samples.

greater significance was the observation that a similar linear relationship was obtained when the percent solids of four different commercial black liquor samples were correlated with the magnitude of the FID signal, as summarized in Figure 3. It is interesting to note that a linear relationship was observed over a wide range of differing types of industrial black-liquor samples. These results suggest that it is potentially possible to develop a stop-flow or an on-line, at-line NMR sensor for determining % solids for black liquor samples, although further studies will be needed to develop this concept.

As previously mentioned, there have been a number of studies examining the use of T_2 measurements to predict solution viscosities. From a theoretical basis, dipolar relaxation is known to be dependent on τ_c, the molecular correlation constant, which is defined as the time it takes for a molecule in solution to reorient itself one radian, and this parameter is dependent upon the solution viscosity.[15] Although several publications have attempted to derive a theoretical relationship between T_2 or T_1 values and viscosity, all of these models have

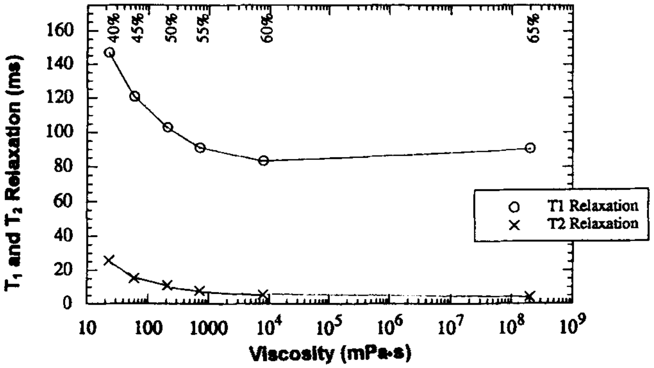

Figure 4. 400 Mhz ^{1}H T_1 and T_2 values of water present in black liquor sample II at five diffeerent dilutions.

limited application.[14,16] From a process control perspective, Snoody's approach of defining a correlation curve between viscosity values for known samples and measured T_2 values appeared to be the simplest and most direct method for pulping liquors.[17] As a preliminary investigation, we measured the proton NMR T_1 and T_2 values for water in each pulping liquor at several % solids levels and these values were correlated to viscosity measurements made independent of the NMR experiment. The results of the 400 MHz studies for pulping liquor I are summarized in Figure 4. Although the general shape of curves was consistent with theoretical considerations, we were unable to establish a general relationship for all four pulping liquors. Undoubtedly, differences in chemical composition, the metals content of the various pulp liquors, and the non-Newtonian behavior of high solids black liquor precluded the generation of a global relationship between viscosity and T_2 relaxation rate constant.

A recent study by Li et al. suggests that NMR viscosity measurement may best be accomplished employing a pulse-gradient approach.[18]

CONCLUSIONS

As anticipated, the proton spectral resolution of kraft black liquor samples using a low-field NMR spectrometer is substantially reduced over routine high-field NMR analysis. Nonetheless, the % solids content of various black liquor samples can be readily determined by using a low-field NMR spectrometer to measure the signal intensity of the overall FID. Although these initial investigations were performed on static samples, it is anticipated comparable results could be achieved with a flow-through cell system since Haw has recently reported that a PAC NMR method could be used to characterize gasoline components using a flow-through cell.[19] These results suggest that a comparable approach could be developed for on-line, at-line NMR analysis of black liquor. Further research into sample cell design, influence of temperature, and other industrial parameters need to be investigated before practical mill applications are to be considered. Nonetheless, our results certainly suggest that future advancements in this field hold promise for further NMR sensor applications in pulp mill operations.

EXPERIMENTAL

Black Liquor Samples

Concentrated pulping liquors were acquired from four different commercial kraft pulping operations: samples I and II were acquired from kraft mills employing an uneven mix of softwood and hardwood; sample III originated from a mill employing 100% softwood; and sample IV came from a mill cooking with a 50/50 mix of softwood and hardwood. The liquor samples were stored at 0°C prior to use and were characterized according to their metals content,

TABLE 1. Physical Properties of Kraft Black Liquor Samples I - IV.

Black Liquor Sample	Viscosity[a]	% Solids[b]	% Elemental Analysis[b] C	H	S	Na	Fe	K
I	11,230	61.48	37.10	4.04	4.01	19.96	>.01	0.83
II	2.0×10^8	65.17	35.99	3.20	4.22	10.89	0.01	0.94
III	12,070	70.72	37.76	3.58	5.44	11.57	0.01	0.96
IV	---	71.60	37.23	3.85	5.30	12.34	>.01	1.79

[a]mPa's measured at 40°C; [b]% solids analysis and elemental analysis of dry black liquor samples were performed by Huffman Laboratories, Inc., Golden, CO.

moisture contents, and viscosity values (see Table 1). The viscosity values were measured with a Brookfield Synchro-Lectric RVT viscometer following Ramamurthy's procedure[20] at several temperatures (40-80°C). Black liquor viscosity values measured at 40°C are summarized in Table 1.

Black Liqour Dilution Procedure

A sample of black liqour, of known % solids, was diluted with deionized water to afford the desired dilution factor. The mixture was then warmed to 40°C and mixed (ca. ½ h) to ensure a homogenous solution.

NMR Studies

Low-field studies were performed on a 60 MHz NMR spectrometer manufactured by Elbit-ATI. Routine ^{1}H NMR acquisition parameters included: 90° pulse, 64 scans/spectrum, 12 s D1 (D1:relaxation delay) , at 40°C, and 8,463

Hz spectral width. The low-field proton NMR measurements were confirmed using a 400 MHz Varian spectrometer with a 35° pulse, 2 s D_1, 8,000 Hz spectral width, at 40°C and 64 scans/spectrum. ^1H NMR T_1 and T_2 values for water in black liqour samples were determined using the standard inversion recovery method and Carr-Purcell-Meiboom-Gill sequences,[21] respectively, on a 400 MHz spectrometer. All spectra were recorded without a lock because the samples were too viscous for an external lock and we did not wish to dilute the samples with a deuterated solvent.

ACKNOWLEDGEMENTS

The support of Ebit-ATI Instruments and Dr. M. Gordon during this project is gratefully appreciated. Portions of this work were used by E.J.D. as partial fulfillment of the requirements for the M.S. degree at the Institute of Paper Science and Technology. The continuing support of the Member Companies of IPST for Ragauskas' research is fully appreciated.

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