APPENDIX B

VISCOSITY OF BLACK LIQUOR PROJECT

(Some NMR Theory and Competing Technologies)
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GENERAL PRINCIPLE

The discussion of magnetic resonance is confined to nuclides with a spin quantum number of 1/2. Many other effects are also ignored for the sake of clarity.

Basic Magnetic Resonance

Magnetic resonance (MR) is a nondestructive, noninvasive technique that arises from the magnetic properties of atomic nuclei. When immersed in a steady magnetic field, $B_0$, the nuclei align with the field and precess (rotate) about it at a characteristic frequency, called the Larmor, or MR frequency. This frequency, $\omega_0$, is related to the steady magnetic field by

$$\omega_0 = \gamma B_0.$$  (1)

The constant $\gamma$ is the magnetogyric ratio, and has a different value for each nuclide. In effect, $\gamma$ determines the MR frequency for a given value of applied magnetic field.

In pulsed MR, an externally applied pulse of radio-frequency (RF) energy at the Larmor frequency causes the nuclei to tip away from their equilibrium position. The spin magnetization may now be detected as it precesses about the static magnetic field at the Larmor frequency. The signal is detected as the current induced in a conducting coil which is itself a part of a circuit tuned to the Larmor frequency.

The magnitude of the MR signal depends upon the magnitude of the magnetization at the time of the pulse. The equilibrium magnetization, $M_0$, in an applied field, $B_0$, is given by

$$M_0 = \frac{N\gamma^2 h^2 I(I+1)B_0}{12\pi^2 kT}$$  (2)

where $I = 1/2$ for protons, $\gamma$ is the proton magnetogyric ratio, $N$ is the total number of nuclei in the sample, $h$ is Planck's constant, $k$ is Boltzmann's constant, and $T$ is the absolute temperature. To provide maximum detection sensitivity in a single pulse MR experiment, the RF pulse must be of sufficient energy to cause the nuclei to be tipped 90 degrees from the applied static magnetic field. This is achieved by making the pulse of sufficient intensity and duration to form what is commonly known as a 90° or $\pi/2$ pulse.

In the evaluation of any MR application, the signal-to-noise ratio (SNR) of the proposed configuration is of primary importance. The SNR of a MR system is a function of a large number of variables and is highly configuration dependent. However, for the purposes of this study, we can fix most of these variables and concentrate only on the most important. For a given configuration, the SNR of an MR system can be represented by the following relationship.
In this expression, \( \rho \) is the density of resonant nuclei in the sensitive region of the system; \( V_i \) is the volume of the sensitive region of the instrument, which is assumed to be filled with the material under study; \( \delta_f \) is the bandwidth of the MR receiver; and \( \omega_0 \) is the Larmor precession frequency (see Eq. (1)). Due to the strong dependence of the SNR on \( \omega_0 \) it is desirable to operate at as high a field as is practical (note that higher field entails increased cost) while observing a nuclide with a relatively large magnetogyric ratio. Since \( \gamma \) for hydrogen nuclei is among the largest of magnetogyric ratios and black liquor contains a high density of hydrogen nuclei, observation of the hydrogen nucleus is the natural choice for MR measurements of black liquor.

**MR Relaxation and Viscosity**

The magnetization created by the initial pulse of the MR experiment described above decays with respect to two different time constants which may be related to distinct processes. These two decay times which are referred to as \( T_1 \) and \( T_2 \) are defined below.

**\( T_1 \):** The spin-lattice relaxation time. The characteristic time for the nuclear spin system to come to equilibrium with its surroundings following a disturbance. Disturbances may be induced by a RF pulse or by a change in the static applied field.

**\( T_2 \):** The spin-spin relaxation time. The characteristic time for the spin system to come to internal equilibrium following a disturbance. It is also the approximate decay time for the MR free induction decay (FID) in a perfectly homogeneous magnetic field.

We will first consider the relationship between the two relaxation times and the viscosity of the fluid. Both of these relaxation times are affected by both inter- and intramolecular motion. This is due to the nature of the spin-spin and spin-lattice couplings which drive the relaxation of the magnetization. Given certain assumptions an analytical relationship between \( T_1 \) and \( T_2 \) and the molecular reorientation time, \( \tau_c \), may be determined. Since the molecular reorientation time is proportional to the ratio of the zero shear viscosity, \( \eta_0 \), to the absolute temperature in Kelvin, \( T_K \), we have a direct relationship between the MR relaxation parameters and viscosity.

The primary assumption made about the fluid in the following discussion is that the individual molecules are undergoing rapid reorientation with respect to the timescale of the interactions (e.g., dipolar or quadrupolar couplings) which cause the MR relaxation. Given this restriction, the MR relaxation rates have been shown to have the following dependence:

\[
\frac{1}{T_i} \propto I(I + 1)[J_1(\omega_o) + J_2(2\omega_o)]
\]  

(4)
\[ \frac{1}{T_2} \propto I(I+1) \left[ \frac{1}{4} J_0(0) + \frac{5}{2} J_1(\omega_0) + \frac{1}{4} J_2(2\omega_0) \right], \] (5)

where \( \omega_0 \) is the Larmor precession frequency, Eq. (1), and

\[ J_0(\omega) = \frac{24}{15r^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2} \] (6)

\[ J_1(\omega) = \frac{4}{15r^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2} \] (7)

\[ J_2(\omega) = \frac{16}{15r^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2}. \] (8)

The variable \( r \) represents the length scale of the MR process responsible for the relaxation and can be assumed to be a constant in our case.

In the limit that \( \omega \tau_c << 1 \) (low viscosity) we have that

\[ T_1 \propto \frac{1}{\tau_c}, \] (9)

\[ T_2 \propto \frac{1}{\tau_c}. \] (10)

On the other hand if \( \omega \tau_c >> 1 \) (high viscosity), then

\[ T_1 \propto \tau_c, \] (11)

\[ T_2 \propto \frac{1}{\tau_c}. \] (12)

Since \( \tau_c \propto \eta/T_K \), there is a direct correlation between the MR relaxation times and the fluid viscosity. Of course, the black liquor fluid is actually composed of fluids and solids which complicates the problem. There should, however, be a strong correlation between the relaxation times and the zero shear rate viscosity.

For the black liquor samples, we expect that the system will be in the fast motion or low viscosity regime (Equations 9 and 10). So for increasing viscosity we expect to have decreasing NMR relaxation times.

Another important fact is the dependence of the viscosity upon temperature, so the correlation time is not strictly inversely proportional to the temperature. Researchers at the
University of Florida in Gainsville have found that the temperature dependence of the viscosity is usually of the form

\[ \ln(\eta) = A_0 + \frac{A_1}{T} + \frac{A_2}{T^2} , \]

where \( A_0, A_1 \) and \( A_2 \) are constants. At present, I am not aware of the physical significance of such a dependence. It could be purely empirical, i.e. just a Taylor expansion in \( 1/T \). The NMR relaxation times may then be written as

\[ \ln(T_1) = \ln(T) + C_1 - \left( A_0 + \frac{A_1}{T} + \frac{A_2}{T^2} \right) \]

\[ \ln(T_2) = \ln(T) + C_2 - \left( A_0 + \frac{A_1}{T} + \frac{A_2}{T^2} \right) . \]

The constants \( C_1 \) and \( C_2 \) are the proportionality constants in Equations 9 and 10.

**KNOWN COMPETITION - RHEOMETERS AND VISCOMETERS**

Viscosity measurements are usually carried out by forcing the fluid to move with respect to some object; the stress created by the movement is then measured and related to the viscosity. Such techniques rely upon a model or some approximation to the fluid motion in order to determine the dynamic viscosity. Other means which monitor time dependent behavior in the fluid may also be used, but at this time we know little about such techniques, so we will focus on the viscometers of the first type.

A number of viscometer types were discussed at the January 1995 meeting in Florida. The viscometers which are currently being tested at the test-loop in Florida are listed below. A brief (and perhaps not entirely correct) description of the operation of each device is included. Information concerning the specifics for the device listed below was obtained in a brief phone conversation with Tony Dutka (University of Florida, Department of Chemical Engineering, Gainsville, FL, 904-392-0072). Note that at this time none of these viscometers are used to monitor black liquor viscosity on-line at an actual processing plant.

Described below are two common types of on/off-line viscometers. The following descriptions of rheometers and rheometer suppliers should not be considered to be in any way complete.

**Rotating Cylinder**

The fluid passes through the gap between two concentric cylinders. One of the cylinders is rotated, and the force required is measured. From the rotation rate and the measured force the viscosity at a given shear rate may be determined. Often, multiple rotation rates are used in order to plot out a shear viscosity vs shear rate curve which contains information concerning the type of flow and the shear independent or apparent viscosity. For a known system, one may potentially determine the apparent viscosity in a single measurement. The
exact method employed by the manufacturer listed below is not known. The system measures an apparent viscosity which must be related to the true viscosity through the use of a model.

**Known Manufacturers & Products**

Brookfield Engineering Laboratories, Inc. - Device currently being tested in Florida. Device cost ~$10,000-$12,000.

**Capillary**

The fluid passes through a small capillary. The mass flow rate and pressure drop are measured. The pressure drop is usually measured with pressure sensitive transducers. A number of means are used to determine the mass flow rate; until further information is obtained on the device(s) listed below, we will not go into the details of measuring mass transport in a capillary. From the tube inner diameter and the pressure and mass flow rate measurements, one may obtain the viscosity for a given shear rate. The device generally utilizes a range of capillary diameters and/or flow rates to determine the shear viscosity vs shear rate curve. From this one may determine the apparent viscosity. The devices being employed at the test flow loop are designed to measure the viscosity at a single shear rate.

**Known Manufacturers & Products**

Micro-Motion, Inc. - Device currently being tested in Florida. Large producer of mass flow meters for gases and liquids. Device cost ~$10,000-$12,000.

**Other**

Nametre Company. - Device currently being tested in Florida. Some type of device employing a vibrating reed to measure some time-dependent response of the fluid. Requires an ancillary sample density measurement. Device cost ~$35,000-$38,000.

**Devices/Companies not mentioned by Tony Dutka**

Rheometrics Scientific, Inc. (Piscataway, NJ) - Rheometrics is perhaps the largest supplier of rheological test instruments both on- and off-line. They are also currently associated with Auburn International Inc. Auburn produces industrial MR devices and currently has an on-line(?) product used by DuPont for the analysis of liquid polymer samples. Information concerning Auburn is contained in the “HT NMR Advanced Moisture Sensor Market Feasibility Analysis”.

**KNOWN COMPETITION - OTHER**

There appears to be little or no use at present of rheometers or viscometers as process control devices for black liquor recovery. This conclusion is based upon discussions with industry and university experts. This is not to say that nothing is used for black liquor process control. The two most common devices used to gain some measure of the black liquor solids content are refractometers and nuclear absorption devices.