NMR

Pore Size Distribution Measured by PGSE NMR and Relaxometry

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Innovation with Integrity

Introduction

Measuring and characterizing the porous structure of porous medias is a challenging yet important task. Porous structure characteristics include pore size, porosity, pore volume, and surface area to volume ratio. Understanding these characteristics is critical for optimized utilization of porous material. Currently, gas adsorption-desorption and mercury intrusion porosimetry (MIP) are the most common methods used to measure pore size distributions. However, these methods are destructive and potentially alter the structure of the material as they require drying the material and introducing probe molecules at high pressures. In contrast, NMR methods are non-destructive and capable of in-situ observation of the solvent of interest. Additionally, NMR methods can be less time-consuming.

To measure the pore size distribution, a combination of Pulsed Gradient Spin Echo (PGSE) experiments and relaxation measurements are utilized. The PGSE experiments in porous medias often require a short, pulsed field gradient duration and therefore strong gradients are required. For this reason, a probe with gradient strengths above 2.5 Tm^{-1} is recommended such as a high-power diffusion probe or an imaging probe with strong gradients.

This application note is based on 'Short-time behavior of the diffusion coefficient as a geometrical probe of porous media' by Mitra, Sen, and Schwartz [1], and 'Absolute Pore Size Distributions from NMR' by Sorland et al.[2] Additional details can be found in these works.

Figure 1: Image of MICRO5 probe base and gradient set with wide bore adaptor.

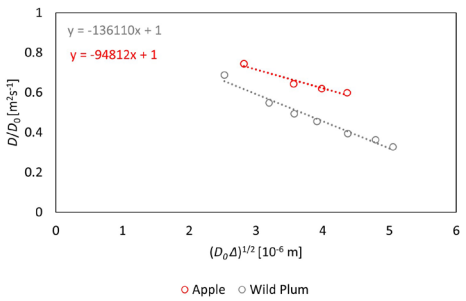

Figure 2: The dependence of the diffusion coefficient (D) of water inside wood samples on the observation time Δ in wood from Apple (red) and Wild Plum (gray) plants. The experimental data shows a larger slope in the plot of D/D_0 as a function of $(D0\ \Delta)^{1/2}$ in a wood sample from a Wild Plum plant as compared to from an Apple plant indicating a larger surface to volume ratio and a smaller average pore size in the wood from a Wild Plum plant than the Apple wood.

Experimental

Two fresh, saturated wood samples were analyzed from the following plants: Apple, and Wild Plum. The samples were cut fresh from the plant and stored in water for 5 days before scanning.

The experiments were performed on an AVANCE III HD spectrometer operating at 500 MHz with a 10 mm ^{1}H coil with a MICRO5 gradient set with a maximum gradient of 3 Tm^{-1} at 60 Amps. To measure diffusion, a Pulsed Gradient Stimulated Echo Sequence (PGStE) sequence [3,4] was used with varying diffusion observation times, Δ. To measure T_2, the Carr-Purcell-Meiboom-Gill (CPMG) sequence [5] was used. Total experiment time for PGStE scans with 8 different Δ times and a CPMG scan was 1 hour.

Results and Discussion

When the diffusion observation time, Δ, is short, the diffusion coefficient of fluid inside in porous media is linearly dependent on the surface to volume ratio of that porous media such that:

$$\frac{D(\Delta)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}}\sqrt{D_0\Delta}\frac{S}{V} \quad (1)$$

where D(Δ) is the diffusion coefficient observed at Δ, D_0 unrestricted diffusion coefficient of the bulk solvent, and S/V is the surface to volume ratio. In a heterogenous system with more than one pore size, this relationship is extended to account for the volume fraction of each population ξi:

$$\sum_i \xi_i \frac{D_i}{D_0} = \sum_i \xi_i [1 - \frac{4}{9\sqrt{\pi}}\sqrt{D_0\Delta}\frac{S}{V}] = 1 - \frac{4}{9\sqrt{\pi}}\sqrt{D_0\Delta}\frac{\overline{S}}{V} \quad (2)$$

Therefore, the slope of the linear fit of D plotted against $(D0\ \Delta)^{1/2}$ is the average surface to volume ratio (Figure 2). In the example shown here, the diffusion of water inside a wood piece from a Wild Plum plant (gray) is faster and shows a greater slope when plotted against $(D0\ \Delta)^{1/2}$ as compared to wood from an Apple tree (red). The S/V ratio is the slope the linear fit and if spherical pores are assumed, the average pore sizes are 5.5 and 7.9 µm for Wild Plum and Apple plant respectively. This is in agreement with results of pores in wood.[6]

NMR relaxation also has a relationship to the surface to volume ratio:

$$\sum_i \xi_i \frac{1}{T_{2,i}} = \sum_i \xi_i \left[\frac{1}{T_{2,bulk}} + \rho_2 \frac{S}{V} + \frac{\gamma^2 G_{0,i}^2 D(2\tau)^2}{12}\right] = \frac{1}{T_{2,bulk}} + \rho_2 \frac{\bar{S}}{V} + \frac{\gamma^2 \bar{G}_0^2 D(2\tau)^2}{12} \quad (3)$$

$$\sum_i \xi_i \frac{1}{T_{1,i}} = \sum_i \varepsilon_i \left[\frac{1}{T_{1,bulk}} + \rho_1 \frac{S}{V}\right] = \frac{1}{T_{1,bulk}} + \rho_1 \frac{\bar{S}}{V} \quad (4)$$

where ρ is the surface relaxivity, γ is the gyromagnetic ratio, G_0 is the background gradient, and 2τ is the time between two 180-degree pulses in the CPMG sequence. When the surface to volume ratio is known from the diffusion experiments and the T_1 or T_2 relaxation time is measured, ρ can be fit once the other terms are considered. In the case of a short τ and well-shimmed system, the third term equation (4) is negligible. If this is not the case, the diffusion term in the T_2 relationship can be determined and incorporated after making measurements of $T_2(2\tau)$. Additionally, when the T_1 and T_2 are long, $T_{1,bulk}^{-1}$ and $T_{2,bulk}^{-1}$ is also negligible. If these conditions are not met, the results of the measurement of the solvent T_1 and T_2 can be incorporated.

To analyse the relaxation data in a system with more than one decaying population, the decay data is fit using the Inverse Laplace Transform[7] in which the y values on the plot correspond to the volume fraction ξ and x values correspond to relaxation values. Using the sum of these two quantities multiplied together to obtain the average relaxation rate, the surface relaxivity ρ can be fit since the average surface to volume term is known from diffusion experiments (Equation (2). Then, the T_2 or T_1 distribution can be converted to a distribution of surface to volume ratios using equations 3 or 4. If short T_2 or T_1 times are observed, relaxation weighting may occur during the diffusion experiment. If this is the case, the ξ values from the ILT should be multiplied by exp ($-2\delta/T_2$) or exp ($-\Delta/T_1$) such that volume fraction observed in the diffusion experiment and relaxation experiments are equivalent. The surface to volume ratios can be converted to pore size by assuming the geometry of the pores.

In these two wood samples (Figure 3), T_2 data shows two components with a distribution of relaxation rates, meaning that there is an underlying distribution of pore sizes in the wood samples that make up the average pore sizes. When the T_2 data is converted to pore size, the Apple wood sample has more large pores with pore radii from 10-16 μm while the wood from a Wild Plum plant has smaller pores with radii from 6-11 μm.

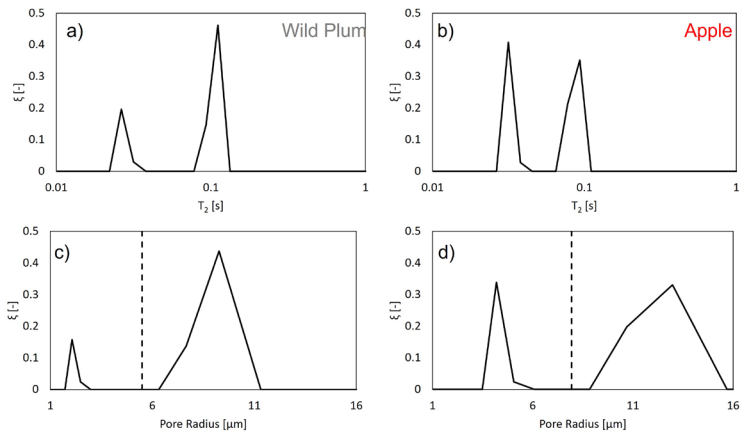

Figure 3: The T_2 distributions of water inside wood from a Wild Plum (a) and Apple (b) plant show a distribution of relaxation rates. These distributions are converted to pore size distributions for the Wild Plum (c) and Apple (d) wood samples using the relationship between relaxation and surface to volume ratio and an assumed pore geometry. The average pore size is shown with the dashed line.

Conclusion

Pulsed Gradient Spin Echo diffusion measurements with high powered gradients allows for the measurements of restricted diffusion and the average surface to volume ratio in complex systems. By pairing these diffusion measurements with relaxation measurements, it is possible to measure the pore size distribution with pores sizes ranging from 1 – 100 µm. The experiments are easy to perform, fast, non-invasive, and do not require tracer molecules such as comparable methods leading to more accurate results.

References

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