Abstract

Production of oil from organic shale reservoirs is a function of porosity, hydrocarbon saturation, pore pressure, matrix permeability, and hydraulic fracture surface area plus fracture conductivity. Hydraulic fracture surface area, porosity, saturations and pore pressure dominate initial production rates. Matrix permeability becomes increasingly important in sustaining production later in time. Permeability measurements to oil from organic shale core samples are not commercially available today. However, permeability to oil is believed to be a function of pore throat size, wettability, and water saturation, the same as a conventional reservoir. This work investigates pore size, wettability, and expelled hydrocarbon volumes using log and core-based nuclear magnetic resonance data from the Eagle Ford Shale focused on the comprehensive evaluation of one well. Comparisons with core porosity measurements, scanning electron microscope images (SEM) and mercury injection capillary pressure tests (MICP) are compared with the nuclear magnetic resonance (NMR) interpretation for calibration and validation. The NMR $T_2$ distribution is partitioned into regions of bound and producible free fluid.

Introduction

The focus of petroleum industry activity in North America has migrated from gas to liquid producing shale in the last 3 to 4 years (Birger, 2011). Production and evaluation models developed for gas production may not be directly applicable to liquid systems because of differences in the properties of the hydrocarbon phase, and differences in the resulting interactions between these fluids and the rock matrix.

Loucks et al. (2012) demonstrated that there are two types of pore systems present in organic shale reservoirs. Kerogen-hosted organic matter pores (OM) and inter/intra particle (IP). Their published pore sizes of OM pores range from around 5 to 750 nm, while IP pore sizes ranged from 10 to 2000 nm. All are primarily within their nanopore size range.

Dry gas is believed to be produced from nanopores that occur within the kerogen fraction of the shale. These pores consist of a thin layer of adsorbed gas at the kerogen-pore interface with compressible gas filling the remainder (Ambrose et al. 2010). As shown by Nelson (2010), the pore throat diameters in organic shale range from roughly 10 to 150 times the size of a methane molecule, which has a diameter of 0.38 nm. The kerogen-hosted pore system is generally regarded as water free, thus, there is minimal permeability reduction, or relative permeability effect, due to pore throats being occluded by capillary water. However, there is some potential occlusion from the layer of adsorbed gas lining the pore throats.
Unlike dry gas systems, depending on temperature and pressure conditions, liquid systems may possess two hydrocarbon phases in situ. In a condensate system within the phase envelope, the effective pore throat size and resulting effective permeabilities will be reduced.

Oil molecules approach or even exceed the size of pore throats in organic shale systems (Nelson, 2010). A minimum pore throat size must be present for a hydrocarbon molecule to pass through it. Furthermore, the viscosity of oil is around 20 times greater than that of gas (McCain, 1990). Higher hydrocarbon viscosity represents an additional challenge when flowing oil through an organic shale matrix because Darcy flow rate, if applicable, is inversely proportional to viscosity.

Bitumen, soluble organic matter, may be a common component in liquids-producing shale (Smith et al. 1980). Bitumen is indistinguishable from oil using standard log analysis because its density and neutron response parameters are similar to those of oil. Bitumen may not be producible in shale reservoirs because of its very high viscosity in combination with small pore throat sizes of the nanopores.

As outlined, liquids-bearing shale reservoirs contain fractions of hydrocarbons that are not producible because the hydrocarbon a) is locked into pores with pore throats that are too small, b) contain pore throats that are occluded by a second fluid such as water or liquid condensate or c) contain very viscous bitumen.

The NMR measurement is made by manipulating hydrogen nuclei contained in water or hydrocarbon. The measured amplitude of the NMR signal is proportional to the amount of hydrogen nuclei. The NMR transverse relaxation time ($T_2$) is the time constant associated with the dephasing of precessing hydrogen nuclei during a NMR measurement sequence. $T_2$ is a function of surface, bulk, and diffusion related interactions at the pore level. The $T_2$ for an individual pore and pore fluid is given by

$$1/T_2 = 1/T_{2\text{bulk}} + 1/T_{2\text{surface}} + 1/T_{2\text{diffusion}}$$

(1)

Surface relaxivity ($T_{2\text{surface}}$) describes the interaction between rock and wetting fluid, and is a function of pore size. Bulk relaxivity ($T_{2\text{bulk}}$) is a function of the viscosity of the fluid. The non-wetting fluid decays at the bulk relaxivity rate. The $T_2$ of the wetting fluid will be dominated by the shorter of the $T_2$ mechanisms, either surface or bulk. Diffusion ($T_{2\text{diffusion}}$) is a function of the diffusivity of the fluid, and can only be measured in the presence of a magnetic field gradient. Since the diffusion mechanism is a function the applied magnetic field gradient, it can be minimized or maximized depending on the measurement objectives. A $T_2$ distribution is used to describe a system that contains multiple pore sizes and fluids.

Total porosity includes all reservoir fluids, while effective porosity includes only the volume of interconnected fluid. Effective porosity is commonly estimated to be equal to the total porosity minus the volume of clay bound water. NMR $T_2$ distributions may be used to partition porosity into free and bound porosity, where free fluids reside in free porosity and bound fluids reside in bound porosity. Bound fluids include clay bound and capillary-bound waters. Traditionally, a $T_2$ cutoff is determined by matching the cumulative porosity of the fully saturated $T_2$ distribution to the bound fluid porosity after centrifuging to air at 100 psi capillary pressure. Typical $T_2$ cutoffs for sandstones and carbonates are around 33 ms, 100 ms, respectively (Straley et al. 1997). This technique is based on the expectation that $T_2$ is dominated by surface relaxivity ($1/T_2 \sim 1/T_{2\text{surface}}$), and that producible fluids reside in larger pore spaces while bound fluids reside in smaller pores. Estimation of clay-bound water volume from the $T_2$ distribution is based on an assumption that clay-bound water has the shortest $T_2$ values in the distribution. The porosity associated with the fastest $T_2$ in the NMR distribution is then correlated with electrical membrane potential measurements of clay bound water to determine the clay bound water’s $T_2$ cutoff. A typical $T_2$ cutoff for clay bound water is around 3 ms (Straley et al. 1997). Figure 1 depicts an interpretation model for water wet rocks containing intermediate to light oil. Typical $T_2$ cutoffs for sandstones (SS), carbonates (LS), and clay bound water are 33 ms, 100 ms, and 3 ms, respectively (Straley et al. 1997).

If the hydrocarbon viscosity is very high, $T_2$ bulk will dominate ($1/T_2 \sim 1/T_{2\text{bulk}}$) and cause the oil signal to overlap with the bound fluid signal.

In a hydrocarbon wet rock where light oil is wetting small pores, $T_2$ surface will dominate ($1/T_2 \sim 1/T_{2\text{surface}}$) and cause the light oil signal to overlap with the bound fluid signal.

The NMR longitudinal relaxation time ($T_1$) is the time constant associated with the alignment of hydrogen nuclei during a
Ozen (2011) observed high $T_1/T_2$ ratios of organic shale cuttings saturated in oil, and low $T_1/T_2$ ratio of organic shale cuttings saturated in water. Thus, $T_1/T_2$ ratio can potentially be used to discriminate pore fluids found in organic shale systems. This work describes the $T_2$ distribution in an organic shale reservoir that produces oil. We partition the NMR $T_2$ distribution into regions of bound and free fluid and relate the physical parameters of interpreted pore size and pore throat size to the $T_2$ distribution.

**Collected data**

Core from an Eagle Ford Shale well was analyzed in detail for this study. Basic and advanced core measurements were collected on 10 core-plugs spaced approximately every 10 ft throughout the lower Eagle Ford Shale. The core points were handpicked to avoid high clay streaks. The 1.5 in x 2.0 in core-plugs had a slight diesel smell presumed to be from the OBM filtrate. The measurements on the 10 plugs began about 14 months after the core was recovered. However, the plugs were in very good condition and as received bulk densities measured as part of this study were comparable to the core analyses performed shortly after recovery.

NMR, SEM, and MICP tests were performed at each sampled core depth. A twin plug from each sampled depth was used for retort-based porosity and saturation measurements. Three of the samples were measured with NMR both prior to and after centrifuging to air at 1000 psi, 140° F for three days to measure moveable fluid.

MICP was measured using a Micromeritics AutoPore IV 9520 mercury porosimeter. The samples were broken in pieces small enough to fit within the glass penetrometers, and the samples were then evacuated under vacuum. Mercury was injected at multiple pressures up to 60,000 psi.

The core NMR data was measured on a GeoSpec2 rock core analyzer from Oxford Instruments, with Q-sense technology for high signal to noise (SNR) performance. Both the resonance frequency (2 MHz) and inter-echo spacing ($TE$) of 0.2 ms for core NMR measurements were the same as those employed by the logging tool used in this well. The core NMR data were measured at room temperature and at reservoir temperature (212° F) using a specially designed core-holder. A pore pressure of 200 psi was maintained with nitrogen gas in order to maintain the liquid phase of the saturating fluids in the core during heating. No confining stress was applied. The NMR response of the core samples before and after heating did not change, indicating that the core samples were not altered by the heating. $T_1$-$T_2$ maps were also generated with a $TE$ of 0.1 ms and 24 log-spaced inversion recovery steps ranging from 0.1 ms to 1000 ms. All core NMR and log NMR data were processed with an assumed Hydrogen Index (HI) of 1.

For SEM sample preparation the shale core samples were broken open perpendicular to bedding to expose a fresh surface similar to a fracture face in the subsurface, and then coated with a thin conductive coating of platinum-palladium. The samples were then examined in secondary electron mode with an FEI Quanta 400F Scanning Electron Microscope equipped with an EDAX energy dispersive X-ray unit for spectral analysis. Information gathered from the SEM includes a qualitative assessment of micro texture, mineral cements, porosity types, and the nature of organic matter.

Log NMR was also collected downhole with a $TE$ of 0.2 ms. The first echo was dropped, however, to eliminate any possible influence of ringing, or potential tool induced noise, on the NMR porosity. Comparisons of core- and log-based NMR were made with the same $TE$ of 0.2 ms with the first echo excluded from the analysis, and at the same sample temperature (212° F). Gamma ray, bulk density, neutron porosity, induction resistivity, and lithology from induced gamma ray spectroscopy logs were also collected.

The study well produced 42 API oil with a GOR of 1450 scf/bbl. The best average three months produced 198 barrels of oil per day with 184,000 standard cubic foot of gas per day.

**Data integration steps**

Several data comparisons were performed to describe the log NMR $T_2$ distribution.

First, a comparison was performed between core NMR $T_2$ derived porosity and retort fluid volumes to ascertain the origins of the peaks within the NMR $T_2$ distribution. The NMR $T_2$ distribution was integrated from the right side of the distribution (at long $T_2$) and matched to retort fluid volumes to establish a cutoff for effective porosity.

Second, a comparison between log and core $T_2$ distributions, measured at reservoir temperature, was performed to identify and quantify potentially expelled hydrocarbon. The log NMR $T_2$ distribution was integrated from the left side of the distribution (at short $T_2$) until the integrated log $T_2$ porosity matched the core NMR porosity. The $T_2$ cutoff that is generated during this procedure is believed to represent the boundary between bound and free fluid.
Third, core $T_1$-$T_2$ maps were examined to infer the pore fluid type (water or oil) contained in the major pore systems based on the relationships observed by Ozen (2011). We observed large differences in $T_1/T_2$ ratio as shown on the $T_1$-$T_2$ maps.

Fourth, we interpreted two well logs with NMR and other advanced measurements. The first well contained 10 plugs from the lower Eagle Ford Shale and none from the upper Eagle Ford. It is the same well from which our suite of core measurements were made and analyzed. The second well contained two core plugs in the lower Eagle Ford Shale and one core plug from the upper Eagle Ford; however, we did not have enough material to perform retort porosity analysis for these two plugs. The core NMR distributions of the second well were similar in overall character to that of the first well.

Fifth, the largest pores observed in SEM were compared to the longest $T_2$ of the log NMR $T_2$ distribution to create a rudimentary transform between pore size and $T_2$ distribution.

Sixth, a comparison between porosity from MICP with log NMR was done. Pore body diameter to pore throat ratio was calculated for the study well.

**Core fluid volumes versus core NMR porosity**

For the case in question, the detectable NMR porosity is a function of the number of hydrogen nuclei residing in molecules that are not bound in a solid matrix. The NMR porosity is equal to the total porosity if the hydrogen index (HI) of the measured component is equal to 1, and, if the hydrogen nuclei relax slowly enough to be detectable. The relaxation times for hydrogen nuclei residing in a mineral matrix are generally too fast to be detectable by the instruments. The gas-filled pore volume in the core is not detectable because the pressurized hydrocarbon gas escaped by the time the samples were measured, and the HI of air is essentially zero. We also assumed the relaxation times of kerogen are too fast to be detectable with the NMR instruments because the kerogen is a solid. Thus, the potential sources of hydrogen from the NMR measurements include water and oil in the pore space, clay bound water, and bitumen (Figure 2).

The retort methodology for porosity and saturation was performed by taking a core sample and heating it in air at predefined temperature steps and measuring the fluid volumes expelled. Pore and capillary water plus residual oil is extracted at a lower temperature than clay bound water and bound hydrocarbon (Handwerger, et al., 2011). We refer to this bound hydrocarbon as bound oil in this paper.
Plotted in track 3 of Figure 3 are liquid volumes from the retort measurements. The water remaining in the core, including the clay bound fraction, averaged 1.0 porosity unit (PU), and had a maximum of 1.9 PU. Also based on retort analysis, the residual oil in the core ranged from 0.8 PU to 1.2 PU. The sum of all fluids excluding the bound oil averaged 1.8 PU and had a maximum of 2.9 PU. The total fluids in the core averaged 4.8 PU, with a maximum of 6.75 PU. The majority of the fluid remaining in the core was bound oil.

Included in track 3 of Figure 3 are two curves that represent core NMR porosity (MRP). Both core NMR porosities were collected at a $TE$ of 0.2 ms, and one did not include the first echo in the processing (MRP $TE$ [ms] $= 0.2$). Both sets of core NMR porosity are much higher than the reported retort porosity which does not include the bound oil. However, after including the bound oil volume, the NMR porosities match fairly well. We conclude that the core NMR porosity is sensitive to the bound oil, clay bound water, and free fluids in the core. The reduction in core NMR porosity after dropping the first echo suggests that short $T_2$ components exist which may not be fully captured by the instrument.

As seen in track 4 of Figure 3, the free oil measured by the retort was much lower than the oil measured by Dean-Stark analysis. However, the sum of bound oil and free oil from the retort matched the Dean-Stark analysis fairly well. Thus, the Dean-Stark porosity includes the contribution from bound oil.

**Core retort volumes versus core NMR $T_2$ distributions**

Figure 4 shows a representative example of core NMR $T_2$ distributions for the study well. Both $T_2$ distributions were collected at a $TE$ of 0.2 ms, and one distribution was processed after dropping the first echo to mimic the log NMR results. Several distinct peaks are observed in the data. The second highest peak at point “B” is consistent with the $T_2$ of clay bound water observed in conventional rocks. The inflections and points at the letter “C” are typically where capillary bound fluids are located in conventional rocks. The largest peak at the letter “A” are very short $T_2$ signal consistent with bitumen (Yang 2012).

To obtain an effective porosity cutoff, we make the assumption that the free fluids have a $T_2$ greater than clay bound water and bound oil. Effective porosity will then include free oil, free water, capillary bound oil, and capillary bound water.

As shown in Figure 4, the removal of the first echo from the NMR processing had minimal effect on the cumulative distribution (from the right) until very short $T_2$. The increase in porosity at short $T_2$ suggests more water and/or oil signal exists, but cannot be fully captured due to instrument limitations. Also, the NMR porosity, including the first echo, is always higher than the retort fluid porosity. This indicates that the core samples may contain more bound oil than the retort could extract, or that the NMR is measuring something at short $T_2$ that is not accounted for in our model.

A large temperature dependence in the $T_2$ (and $T_1$) distributions of the core samples was observed (Figure 5). The log-mean $T_2$ doubled upon heating from room temperature to reservoir temperature (212° F), plus the shape of the $T_2$ and $T_1$ distributions changed significantly over most of the sampled depths. The change in shape suggests that some of the underlying components in the distribution (bound oil, clay bound water, oil and pore water) may have different temperature dependencies. In order to understand this further, the various components for $T_2$ relaxation were broken into:
In the case of core NMR, the diffusion relaxation term $T_{2\text{diffusion}}$ does not exist because the relaxation data is acquired without an applied magnetic field gradient, and the internal magnetic field gradients are found to be negligible. In the case of NMR borehole logs, calculations show that $T_{2\text{diffusion}} > 1000$ ms; this can also be neglected when compared with the observed $T_2$ values.

For the purposes of the bulk fluid component, there are three types of fluids present: water, oil and bound oil. In the case of bound oil, the bulk relaxation term $T_{2\text{bulk}}$ dominates the observed $T_2$, and the temperature dependence is given by:

$$1/T_{2\text{bulk}} \sim \eta/T$$  \hspace{1cm} (2)

where $\eta$ is fluid viscosity and $T$ is temperature. In the case of bound oil, Equation 2 takes on a modified power law (Yang 2012), and $T_2$ is reported to increase by a factor of 10 upon heating over the temperature range reported here.

In the case of water and the produced 42 API oil, the bulk relaxation term can be neglected since $T_{2\text{bulk}} > 1000$ ms is much larger than the $T_2$ observed in the core data. For the log data, the $T_2$ observed were generally less than several hundred ms (except at one sampled depth) and, therefore, to a good approximation $T_{2\text{bulk}}$ can also be neglected. Importantly, this suggests that all the saturating fluids are wetting the rock surface. The dominant component for water and light oil in Equation 1 is, therefore, the surface relaxation term given by:

$$1/T_{2\text{surface}} = \rho_2 S/V$$  \hspace{1cm} (3)

where $S/V$ is the surface to volume ratio of the pores, and $\rho_2$ is the surface relaxivity parameter for $T_2$. A temperature dependence in $\rho_2$ was previously reported in certain conventional reservoir rocks, which was accounted for by two-dimensional translational diffusion of the oil or water molecule on the pore surfaces (Godefroy, 2001). In his model, the molecules undergo surface relaxation as they encounter fixed paramagnetic impurities on the pore surface, and the temperature dependence is given by (Godefroy, 2001):

$$\rho_2 \sim \tau_m(T)$$  \hspace{1cm} (4)

where $\tau_m$ is the translational correlation time associated with individual molecular jumps at the pore surface. The temperature dependence $\tau_m(T)$ is modeled with an activation energy law, which for the data reported here yields an activation energy of roughly $\Delta E \sim 2$ kcal/mol, consistent with those reported previously (Godefroy, 2001).

$$1/T_2 = 1/T_{2\text{bulk}} + 1/T_{2\text{surface}} + 1/T_{2\text{diffusion}}$$  \hspace{1cm} (1)
Because of the temperature dependence of the NMR distribution, an effective porosity cutoff was generated for both heated and ambient conditions using the procedure described above. The results are plotted in Figure 6. Three of the low porosity results were removed as there was not enough fluid measured to obtain an accurate result. The $T_2$ cutoff for effective porosity increased from 3.7 ms at ambient conditions to 6.4 ms at reservoir temperature.

The results suggest that log NMR can be used to estimate effective porosity in organic shale reservoirs. NMR measured total porosity could be problematic however because NMR may not measure low enough $T_2$ to fully quantify the bound oil.

**Log NMR $T_2$ distribution versus core NMR $T_2$ distribution**

In the following procedure, we estimate a $T_2$ cutoff to discriminate between free and bound porosity.

The cores were spun to air in a high speed centrifuge with an inlet capillary pressure of 1000 psi and a temperature of 170° F. Reservoir temperature of 212 ° F could not be reached due to equipment limitations, so the temperature was increased as close as possible to reservoir temperature. No fluids were produced after three days of spinning, and core NMR confirmed no change in porosity or $T_2$ response. This null result suggests that all the free fluid escaped the sample during core retrieval. In other words, the core NMR signal reported here is all bound fluid—bound oil and clay-bound water.

The fact that no fluid was produced after spinning the rock for three days can be used to estimate an upper bound for the mobility of the remaining bound fluid in the rock. Using Darcy’s law and assuming a resolution of 0.1 cc for the centrifuge, an upper bound of 2.5 nD/cP for the mobility of the bound fluid was determined. For oil with a viscosity of 0.4 cP this leads to a permeability of 1 nD.

**Table 1: $T_2$ cutoffs in the Eagle Ford Shale**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$T_2$</th>
<th>Dependence on sample temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective porosity</td>
<td>&gt; 3.5 ms to 5.5 ms</td>
<td>Yes</td>
</tr>
<tr>
<td>Clay Bound Water &amp; Bound Oil</td>
<td>&lt; 3.5 to 5.5 ms</td>
<td>Yes</td>
</tr>
<tr>
<td>Free fluid (oil) in OM pore</td>
<td>&gt; ~ 10 ms</td>
<td>Yes</td>
</tr>
<tr>
<td>Bound oil, residual oil</td>
<td>&lt; ~ 10 ms</td>
<td>Yes</td>
</tr>
<tr>
<td>Free fluid in IP pore</td>
<td>&gt; 100 ms</td>
<td></td>
</tr>
<tr>
<td>Capillary bound water in IP</td>
<td>&lt; 100 ms</td>
<td></td>
</tr>
</tbody>
</table>
The assertion that the remaining core NMR signal represented only bound fluid is also used to estimate a $T_2$ cutoff for the log data. Figure 7 shows a comparison of the log response (green) to the core response (red). Assuming that the total core NMR porosity is the bound fluid volume, a $T_2$ cutoff is calculated at each depth by matching the cumulative log porosity starting from the left (low $T_2$) to the total core porosity value. An average $T_2$ cutoff of 9.4 ms was calculated from the log-mean over all depths.

Loucks et al (2012) demonstrated that there are inter-and intra particle pores in organic shale reservoirs. In our investigations using $T_1/T_2$ ratios, we have interpreted the IP pore system to be mixed to water wet. Water wet carbonate reservoirs typically have a $T_2$ cutoff between capillary bound and free fluids of around 100 ms (Straley, 1997). The Eagle Ford Shale mineral matrix is primarily carbonate, thus it is logical to apply the same cutoff of 100 ms to discriminate between the free and bound porosity in the IP pore space. A summary of $T_2$ cutoffs found for the Eagle Ford Shale are listed in Table 1.

**Identification of core pore fluids using $T_1/T_2$ ratio**

Core $T_1$-$T_2$ maps were examined to infer the pore fluid type contained in the pore systems. We observed large differences in $T_1/T_2$ ratio as shown on $T_1$-$T_2$ maps.

The left plot in Figure 8 shows a representative example of a $T_1$-$T_2$ map from core at ambient conditions. Four peaks can be identified on the map with different $T_1$ and $T_2$ values. The right plot shows the calculated $T_1/T_2$ ratio of these four peaks. The two points on the left have $T_2$ values shorter than 10 ms, which is considered bound fluid. The other two points on the right have $T_2$ values longer than 10 ms, which might be producible fluid in larger oil wet pores, or capillary bound water in the IP pore system. It is also observed that two of the four points have relatively higher $T_1/T_2$ ratios than the other two points. If the same method has been applied to all the core samples, four groups of fluids are shown in Figure 8 (from left to right):

<table>
<thead>
<tr>
<th>Group</th>
<th>$T_2$ range</th>
<th>$T_1/T_2$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 ms -0.3 ms</td>
<td>around 10</td>
</tr>
<tr>
<td>2</td>
<td>1 ms -10 ms</td>
<td>around 5</td>
</tr>
<tr>
<td>3</td>
<td>10 ms -20 ms</td>
<td>around 10</td>
</tr>
<tr>
<td>4</td>
<td>around 50 ms</td>
<td>2-3</td>
</tr>
</tbody>
</table>

The $T_1/T_2$ ratios of the first and third groups are about twice that of the second group.

Bound oil (bitumen) has a relatively high $T_1/T_2$ ratio (Yang 2012). The fluid in group 1, with $T_2$ 0.1 -0.3 ms and $T_1/T_2$ ratio of around 10 is interpreted as bitumen because its short $T_2$ is consistent with the bulk relaxivity of bitumen, and it has a high $T_1/T_2$ ratio. As noted previously, retort core analysis reported significant volumes of bound oil.
In group 3, fluid with $T_2$ of 10-20 ms also has $T_1/T_2$ ratio around 10. However, despite possessing a high $T_1/T_2$ ratio, this cannot be bitumen because the $T_2$ is long when compared to the bulk relaxivity of bitumen. In Ozen’s (2011) thesis, organic shale has a $T_1/T_2$ ratio of 1.54 – 2.95 for water saturated organic shale. The $T_1/T_2$ ratio of oil is larger, where $(T_1/T_2)_{oil}/(T_1/T_2)_{water}$ is 1.39 - 1.92. Based on Ozen (2011), the two groups of fluids with $T_1/T_2$ ratio around 10 are identified as oil (green points) and the other two groups are water (blue points).

In Figure 9, the green line separates the oil and water based on $T_1/T_2$ ratio; the blue line ($T_2 = 3$ ms) classifies clay bound water; the pink line ($T_2 = 10$ ms) distinguishes free OM porosity and bound OM porosity. From left to right, the first group of fluid with very short $T_2$ and high $T_1/T_2$ ratio is bitumen or oil in small OM pores; the second group, with $T_2$ around 3 ms and lower $T_1/T_2$ ratio, is clay bound water; the third group with relatively longer $T_2$ and high $T_1/T_2$ ratio is oil in large OM pore; the last group with even longer $T_2$ with low $T_1/T_2$ ratio 2-3 is water in IP pore.

The $T_2$ values for all the fluids are less than 100 ms. This is a much shorter $T_2$ when compared to the bulk $T_2$ of water and the 42 API oil produced from this well. This indicates the $T_2$ is surface relaxation dominant and all the fluids are wetting the rock. It has been reported that the $T_1/T_2$ ratio increases as the surface concentration of paramagnetic ions increases in the rock matrix (Foley 1996). This may suggest that the clays have a larger paramagnetic ion concentrations than the IP matrix. The high $T_1/T_2$ ratio of oil in OM pore could also be due to the higher surface concentration of paramagnetic ion from the organic coated material on the surface of the OM pore.

Another possible reason for variations in $T_1/T_2$ ratio could be the surface enhanced dipole-dipole interaction (Hirasaki 2008) between oil and OM pore surface. For surface enhanced dipole-dipole interaction induced relaxation, surface relaxivity of both oil and water will decrease with temperature (Straley 2002, Chen 2005). In this case, the $T_2$ distribution will shift to longer relaxation times at higher temperature; however the maximum theoretical effect is limited (Foley 1996).

Yet another explanation for variations in $T_1/T_2$ ratio could be due to differences in the various correlation times associated with 2-D surface diffusion of wetting molecules in the presence of paramagnetic surface sites (Godfrey, 2001). As mentioned above in Equation (4), this model could also account for the observed temperature dependences in $T_1$ and $T_2$. 

Figure 9: $T_1/T_2$ ratio vs. $T_2$ of 10 core samples from core NMR measurement at ambient conditions
Application of $T_2$ cutoffs to log data

Log Example 1

The log data for the study well are plotted in Figure 10. The density (DPHI-LS) and neutron porosity (NPHU_EC) are computed on a limestone matrix and presented in track 4 with magnetic resonance porosity (MRP_CMR). Pore fluids, bound oil, and kerogen all have low fluid or matrix densities, so are typically interpreted as porosity with the density tool. The NMR tool responds only to reservoir pore fluids and bound oil with relaxation times long enough to be measured. The inorganic rock has a matrix density similar to limestone (2.71 g/cc). Hence, there is a noticeable difference between magnetic resonance porosity and density porosity in this example. By applying a $T_2$ cutoff at 5 ms, the clay bound water and bound oil signal may be removed, and thus the effective porosity can be estimated as seen in track 6.

Plotted in track 8 of Figure 10 are free fluids with a $T_2$ relaxation greater than 10 ms. Capillary bound fluids in the intergranular pore system are found between a $T_2$ of 3 ms to 100 ms. There is some overlap between the $T_2$ signature of free oil in the organic matter pore system and capillary bound water in the intergranular pore system. However, because the water saturation is low as indicated by the resistivity log, it is interpreted that the majority of the fluid with a $T_2$ of greater than 10 ms is free oil.

The zone with highest reservoir quality in Figure 10 is at xx30ft where the free oil volumes are the greatest and average around 3.5 PU. There is also an indication of up to 1 PU of conventional porosity plotted ($T_2 > 100$ ms) in track 9. The free fluid porosity represents an upper bound of recoverable oil. Therefore, the free fluid porosity may be used as an index to help evaluate well stimulation performance by comparing it with the produced oil volume.

Bound fluids include clay bound water; capillary bound water and oil and bound oil (bitumen). In this analysis, over half the hydrocarbon in place is bound oil. Log and core analysis methods that do not take bound oil into account may be extremely misleading.

![Figure 10: Log data of the study well with $T_2$ cutoffs applied. Plotted log data includes gamma-ray, density-porosity (DPHI-LS), neutron-porosity (NPHU-EC), inductive-resistivity, and lithology from induced gamma-ray spectroscopy (WPYR, WCAR, WQFM, and WCLA); which represent the weight percent of pyrite, carbonate, quartz+feldspar+mica, and weight of clay respectively. Nuclear porosity values are with limestone matrix. Tracks 6, 7, 8, and 9 include effective, bound, free, and conventional fluid volumes.](image-url)
Log Example 2

Measurements from a different Eagle Ford Shale well with an identical logging suite are presented in Figure 11. As seen in track 8, porosity with a $T_2$ greater than 10 ms is higher in the upper Eagle Ford than the lower. However, the resistivity and density porosity are lower in the upper Eagle Ford compared to the lower Eagle Ford implying a higher water saturation in the upper. Assuming the organic matter porosity is water free, the IP pore space must be proportionally greater in the upper Eagle Ford. Most of the water is interpreted as capillary bound, however, as there is very little increase in porosity greater than 100 ms.

In wells with similar log responses, quantities of more than 2 weight% total organic carbon (TOC) are routinely recorded via pyrolysis techniques. In this well, unlike the previous example (Figure 10), the density porosity matched the log NMR porosity over much of the upper Eagle Ford strongly suggesting that kerogen was not measured by the NMR logging tool. If kerogen is present, the density porosity should read higher than the NMR porosity except in the presence of heavy minerals. Because there are not enough heavy minerals present in the upper Eagle Ford to significantly reduce the density porosity, we interpret that TOC from pyrolysis-based analyses includes bitumen in the measured TOC fraction.

Figure 11: Log data of a second well that includes the upper Eagle Ford Shale. Capillary bound water increases in the upper Eagle Ford shale resulting in an increase in porosity with a $T_2$ greater than 10 ms. The NMR porosity in the upper Eagle Ford matches the density porosity for much of the log implying less kerogen.
Log NMR $T_2$ distribution versus SEM

SEM images from each sample depth were analyzed. Displayed upper-left in Figure 12 (sample depth xx81 ft, near bottom of lower Eagle Ford) is a 8 by 8 μm SEM image illustrating spongy kerogen (ke) that hosts small (OM) nanopores that are in the tens of nm in size (yellow arrow). At upper-right in figure 12, (sample depth xx10 ft, upper part of lower Eagle Ford) is another SEM image that exhibits larger OM pores. The right edge of the $T_2$ distribution corresponds to the largest pores at upper-right. It has been shown through the comparison of log and core NMR that oil is predominately produced from the largest pores. Also, because we observe very little fluid relaxing at the bulk relaxivity rate of 42 API oil ($T_2 \sim 1000$ ms), we know the pores are most likely monophasic, and thus the OM pores displayed in Figure 12 are believed to be oil wet.

![SEM images from each sample depth.](image)

Figure 12: $T_2$ distribution from log (green) compared with SEM. The right edge of the $T_2$ distribution is 70 ms at the depth of xx10ft. The largest pore diameter observed in the SEM at the same depth is 1750 nm.

<table>
<thead>
<tr>
<th>Table 2: Estimated minimum producible pore size</th>
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<tr>
<td>Observed Pore Diameter (μm)</td>
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<tr>
<td>1.75</td>
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<tr>
<td>Carbonate (Marschall et al. 1995)</td>
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<tr>
<td>Sandstone (Marschall et al. 1995)</td>
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</table>

Inputs to calculate the surface relaxivity parameter, $\rho_2$, were estimated by correlating the right edge of the $T_2$ distribution to the largest pore sizes observed in the SEM from the same depth (Figure 12). Equation 3 was then used to obtain the results in
Table 2. Pore size at the free fluid cutoff (10ms) suggests that producible pores are around 252nm or greater. The surface relaxivity, $\rho_2$, is estimated at 4.2 $\mu$m/s and is consistent with 5 $\mu$m/s reported by Ozen (2011).

Log NMR $T_2$ distribution versus MICP

Ten shale core samples were also subjected to drainage only MICP measurements. The median pore throat diameter is estimated to range from 10 nm to 35 nm with equivalent mercury injection pressures of 6943 psi to 22,294 psi (Figure 13). Average pore throat size for the 10 samples was 16.9 nm. The lowest porosity samples had the highest pore throat size (sample 9 and sample 7).

The mercury appeared to saturate even the smallest pores of the samples as the MICP porosity was consistent with both retort effective porosity and porosity above a $T_2$ cutoff of 3ms as seen in Figure 14. These volumes do not include clay bound water and bound hydrocarbon volumes as defined by a NMR $T_2$ cutoff of 3 ms.
The logarithmic mean of the $T_2$ distribution (T2LM) was then calculated for NMR porosity $> 3$ ms. The mean T2LM is 8.77 ms. Equation 3 was then used to obtain an average pore diameter of 221 nm. Since the average pore throat diameter reported from the mercury injection is 16.9 nm, we obtain a pore body to throat ratio (BTR) of 13.1. The average pore throat diameter from the mercury injection tests was plotted against T2LM, and shows relatively good agreement. Because permeability is a function of pore throat diameter, the correlation of T2LM and pore throat diameter suggests NMR can be used to calculate permeability in organic shales.

Conclusions

Well

1) The primary well in the study has 3 to 4 PU of free oil with highest values near the upper third of the lower Eagle Ford Shale.
2) The second well in the study had 1 to 2 PU of free oil with the highest values in the upper half of the lower Eagle Ford Shale.
3) Over half of the hydrocarbon in the lower Eagle Ford Shale is bound oil, which we interpret as bitumen, and is probably not producible.
4) Producible oil in the lower Eagle Ford Shale appears to come from pores that have a diameter of 250 nm or greater.
5) The median pore throat diameter is estimated to range from 10 nm to 35 nm with equivalent mercury injection pressures of 6943 psi to 22,294 psi.
6) The mean pore body to throat ratio for the Lower Eagle Ford is estimated to be 13.1.
7) The upper Eagle Ford Shale in the interpreted well appears to have a much higher fraction of capillary bound water in intergranular pores than the lower part of the shale.
8) There appears to be a significant fraction of bitumen in the upper Eagle Ford that may be included in TOC as measured with pyrolysis methods. A retort core analysis is able to differentiate this bitumen as bound hydrocarbon.

Core and Log

1) Free oil in OM pores has a $T_2$ signature of greater than 10 ms.
2) Bitumen is indistinguishable from oil using standard log analysis methods. Log and core analysis methods which do not take into account bitumen can be extremely misleading.
3) The total porosity measurement from log NMR will be an underestimate because the relaxation times of the bitumen may or may not fall into the measurements range.
4) Log NMR is useful in quantifying effective porosity and identifying the presence of bitumen.
5) Capillary bound water and free oil in organic matter porosity have a similar $T_2$ signature. Resistivity logs can be helpful in differentiating these liquids.
6) Surface relaxivity for the lower Eagle Ford is estimated to be 4.2 $\mu$m/s.
7) Mercury injection porosimetry appears to be provide a representative measure of effective porosity.
8) Pore throat diameter appears to correlate to T2LM calculated above 3 ms and suggests log NMR can be used to calculate permeability in organic shales.

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