A NEW EXPERIMENTAL PROCEDURE FOR NMR HTHP MEASUREMENTS OF CRUDE OIL SAMPLES IN THE OXYGEN-FREE STATE

G.Q. Zhang, J. Ren, H.T. Kwak, C. Edwards and S. Chen
Baker Hughes Incorporated

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Abu Dhabi, UAE, 5-9 October, 2004

ABSTRACT

NMR experiments on sealed hexadecane and light crude oil samples show an increase in the transverse relaxation time after the samples are heated from ambient conditions to 120°C. This increase occurs over the course of many hours after thermal equilibrium is reached. A similar increase for heavy oils is not observed. Upon cooling, the samples retain longer relaxation times at every temperature than similar samples that have not been heated to 120°C. The differences in relaxation times between these samples disappear when the samples are then exposed to air.

Relaxation spectra of heated crude oil samples are consistent with relaxation spectra from oxygen-free samples that were prepared using the conventional freeze-thaw method. Thus, the change in T_2 appears to be related to the amount of dissolved oxygen in the oil samples. Two mechanisms for oxygen removal by heating are suggested: (1) A reduction in solubility of oxygen in the crude oil drives the oxygen out of solutions, and (2) a chemical reaction consumes the oxygen.

A new experimental procedure is proposed based on these observations. Measurements on oxygenated crude oil samples can be made as the samples are heated in steps from ambient conditions to reservoir conditions. Once the samples have reached and remained at 120°C for a period of time, measurements in the oxygen-free state can be made on as the temperature is lowered in steps back to ambient conditions. This simple procedure replaces the conventional freeze-thaw method of producing oxygen-free samples.

INTRODUCTION

NMR is a valuable technique for evaluating reservoir fluid properties both downhole and in the laboratory. Downhole NMR measurements are usually limited to transverse relaxation time, T_2, distributions, but spin-lattice relaxation times and diffusion measurements can be made under special circumstances. Because the relaxation process in crude oils is dominated by the intra-molecular dipole-dipole interaction, a correlation exists between T_2 and viscosity. [1-3] This correlation depends not only on viscosity, but also on temperature, pressure and the amount of dissolved gases. [1]

The relaxation times of hydrocarbons can also be affected by the presence of paramagnetic impurities, usually in the form of dissolved molecular oxygen. T_2 can be greatly reduced by O_2, especially for light crude oils. [1, 4] Normally, native oils are oxygen-free, but circulating drilling fluids may bring oxygen from the surface to the formation, where it could be absorbed by the formation fluids. Measuring the crude oil properties in both the oxygen saturated and oxygen-free states under reservoir conditions is important to NMR log interpretation. If oxygen enhanced T_2 values are used, crude oil viscosity estimates will be erroneous. Thus, laboratory NMR measurements of crude oils should include measurements with and without dissolved oxygen.

The current approach is to use the freeze-thaw method. [3] Several freeze-thaw cycles are necessary and for that reason it is very time consuming. There is also the issue of maintaining the oxygen-free state while transferring treated samples to the high-temperature high-pressure (HTHP) sample chamber for NMR measurements. For these reasons, we have developed a simple procedure to achieve the oxygen-free state without extensive sample preparation. With this new procedure, a single sample can be used to obtain NMR measurements at HTHP in both oxygen saturated and oxygen-free states.

EXPERIMENTAL DETAILS
Pure hexadecane and a number of crude oil samples were studied. The samples included 12.6 API gravity oil as a heavy oil example and 57.4 API gravity oil as a light oil example.

First, a liquid hydrocarbon sample was loaded into a sample chamber and assembled in the HTHP NMR apparatus. The sample chamber was heated and pressurized by circulating a pressurized fluid heated to the desired temperature. T_2 measurements were performed to monitor the temperature equilibrium process. Usually the sample temperature reached equilibrium in less than 2.5 hours. After the temperature stabilized, CPMG T_2 measurements were performed at several pressures to obtain the T_2 pressure dependence.   This sequence was repeated at a number of stepwise increasing temperatures.   Finally, the sequence was repeated as the temperature was reduced stepwise to ambient. The experiments were performed at 2 MHz in Maran Ultra bench top NMR spectrometers.

RESULTS AND DISCUSSION
Figure 1 shows the time dependence of logarithmic mean transverse relaxation time, $T_{2,LM}$, for two hexadecane samples. The first hexadecane sample (shown in Figure 1(a)) was heated stepwise from ambient condition to 30, 60, 90, and 120°C. The time profiles were recorded after thermal equilibrium was reached. For 30°C and 60°C, $T_{2,LM}$ remained unchanged over time. However, for 90°C , after reaching the equilibrium temperature, $T_{2,LM}$ continued to gradually increase until it reached 2400 msec. after about 17 hours. The increase in relaxation time can not be accounted for by the thermal equilibrium process. We propose that the increase in T_2 is caused by the depletion of O_2 dissolved in the hexadecane sample. We suggest as one possible mechanism that as the sample is

heated, the solubility of O_2 decreases [5, 6] and the concentration of O_2 in the sample is reduced causing the increase in T_2. Another possible mechanism is a chemical reaction that consumes the O_2. This accounts for the behavior at 120°C. Once the sample is depleted of O_2 at 90°C and heated to 120°C, $T_{2,LM}$ only increased during the thermal equilibrium process. Figure 1(b) illustrates another series of experiments using a fresh, oxygen saturated hexadecane sample after each time profile was collected. The time profiles were recorded after thermal equilibrium was reached. As temperature increased from 90°C to 120°C, the rate of oxygen depletion increased.

The solubility of oxygen in crude oils should be on the same order of magnitude as that for hexadecane. Thus, the effect of oxygen on the apparent T_2 of light crude oils should be similar to its effect on hexadecane. Figure 2(a) shows the time dependence of $T_{2,LM}$ for the light crude oil sample heated stepwise from ambient temperature to 30, 60, 90, and 120°C. After thermal equilibrium was established ($t < 1$ hr.), $T_{2,LM}$ for the samples at 30°C and 60°C remained constant. $T_{2,LM}$ at 90°C exhibited a slight increase during the experiment. However, $T_{2,LM}$ for the sample at 120°C increased from 2800 to 6400 msec. and became constant after about 7 hours. Similar to hexadecane, rate of oxygen depletion is temperature dependent for the light crude oil sample, as shown in Figure 2(b).

Figure 3 compares $T_{2,LM}$ of samples of the light crude oil example heated to 120°C, cooled to 60°C, and then to 30°C, to the samples heated from ambient to 30°C and then to 60°C. Presumably, the cooled samples remained in the oxygen-free state while the other samples contain O_2. The cooled samples have a $T_{2,LM}$ that was much longer than the samples heated from ambient. At 60°C, the relaxation time is 3700 msec. as compared to 1600 msec. for the heated only sample. A similar comparison can be made at 30°C. The relaxation time for the cooled sample showed a slight decrease over time, but remained at its elevated levels suggesting that once the oxygen-free state is established at high temperature, it can be sustained as the sample is cooled.

Either suggested mechanism can account for samples remaining oxygen-free upon cooling. It is apparent, that if the dissolved oxygen is consumed by a chemical reaction, a sealed sample will remain oxygen free. However, if the oxygen comes out of solution at high temperatures, it will remain in the gas head-space of the sample. Upon cooling, the solubility of the gas increases and the gas in the head-space will dissolve back into the sample. The time required for the oxygen to diffuse into the sample is $\tau_D = L^2/2D$, where L is the sample size and D is the diffusion constant of oxygen in the solution. For the samples we used, $\tau_D \cong 3$ days. This may account for the slight decrease seen at 90°C in Figure 3.

In order to confirm that the sample was oxygen-free after it was heated to 120°C, a sample of the light crude oil was de-oxygenated with the freeze-thaw method. A T_2 measurement was performed to monitor the level of residual O_2 after each cycle. It took three to four freeze-thaw cycles to completely remove the oxygen from a sample about 2 ml. Figure 4 displays four different normalized T_2 relaxation time distributions measured

at the ambient conditions. The solid line is the T_2 distribution of the original crude oil sample. It overlaps with the long-dashed line, which is the T_2 distribution of the sample that was heated to reach the oxygen-free state, cooled to ambient conditions, and finally exposed to air. The short-dashed line represents T_2 distribution of this sample before it was exposed to air and presumed to remain in the oxygen-free state. The solid circles are the T_2 distribution of a sample of the oil after oxygen removal by the conventional freeze-thaw method. These last two T_2 distributions are almost identical, demonstrating that the amount of oxygen in the heated sample and the sample de-oxygenated by the freeze-thaw method was comparable.

Because the relaxation time of heavy oil is small, the intra-molecular dipole-dipole interaction becomes the dominant mechanism. Therefore, the effect of O_2 on T_2 should be negligible.

These experimental results suggest a new experimental procedure to study the NMR T_2 properties of light oils at both the oxygen saturated and oxygen-free states. This can be achieved without using the time consuming freeze-thaw method to remove the oxygen. NMR properties of oxygen saturated samples can be measured as the temperature is stepwise increased. The oxygen-free properties can be measured as the temperature is stepwise decreased once the sample has been maintained at 120°C overnight.

CONCLUSIONS
For the heavy-to-medium crude oils, T_2 does not change at the constant temperature and pressure over time in the temperature range from 30 to 120°C because T_2 is dominated by the intra-molecular dipole-dipole interaction. On the other hand, T_2 is substantially different before and after a sample is heated to 120°C for the medium-to-light oils. We attribute this effect to oxygen depletion when the crude oils are heated to 120°C. We confirmed that the heated samples were oxygen-free by comparing their relaxation spectra to those obtained by the conventional freeze-thaw de-oxygenation method. Therefore, a new experimental procedure is available to measure NMR T_2 properties at both oxygen saturated and oxygen-free states with minimum amount of preparation and experimental time.

ACKNOWLEDGEMENTS

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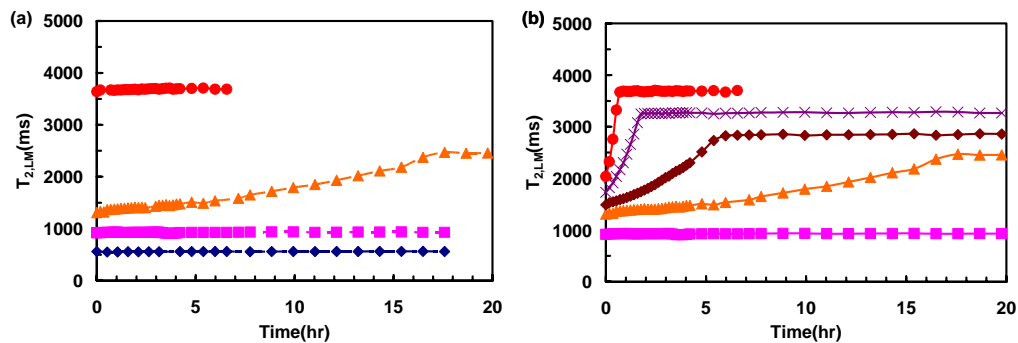
FIGURES

Figure 1: **(a) Time profile of $T_{2,LM}$ of the n-Hexadecane heated stepwise from ambient condition to 30°C (◆), 60°C (■), 90°C (▲), and 120°C (●) at 3000 psi. (b) Time profile of $T_{2,LM}$ of the n-Hexadecane heated from oxygen saturated sample at ambient condition to 60°C (■), 90°C (▲), 100°C (◆), 110°C (×), and 120°C (●) at 3000 psi.**
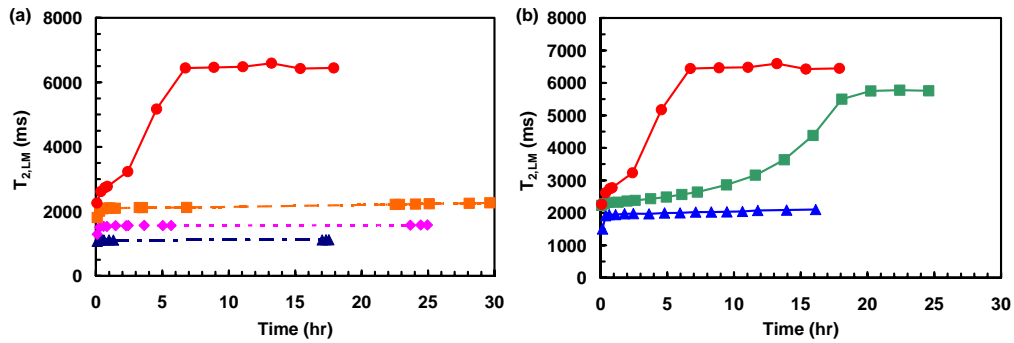
Figure 2: (a) Time profile of $T_{2,LM}$ of the light crude example heated stepwise from ambient condition to 30°C (500 psi) (▲), 60°C (1000 psi) (◆), 90°C (1000 psi) (■), and 120°C (3000 psi) (●). (b) Time profile of $T_{2,LM}$ of the light crude example heated from oxygen saturated sample at ambient condition to 100°C (▲), 110°C (■), and 120°C (●) at 3000 psi.
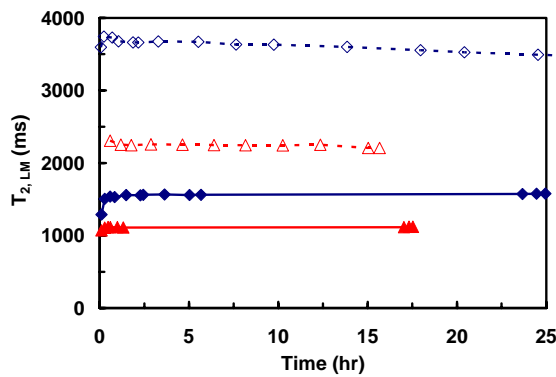

Figure 3: Comparison of $T_{2,LM}$ for light crude oil samples during the heated from ambient to 30°C (▲),60°C (◆), and samples heated to 120°C and then cooled 30°C (△), and 60°C (◇).
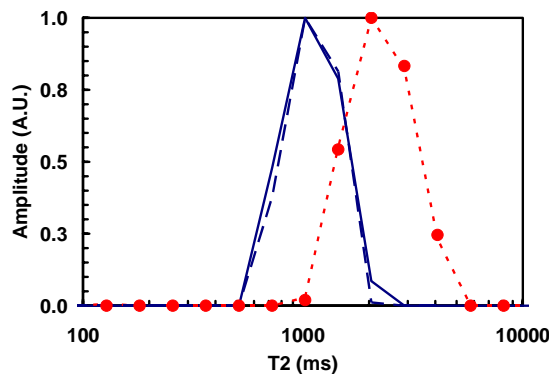

Figure 4: Normalized T_2 relaxation time distributions for the light crude oil example at ambient conditions. The solid line is the initial T_2 distribution. The short-dashed line is the T_2 distribution after the sample is heated to 120°C and cooled to ambient temperature. The long-dashed line is the T_2 distribution after this sample was exposed air. The closed circles (●) are the T_2 distribution when the freeze-thaw method was used to remove its oxygen.
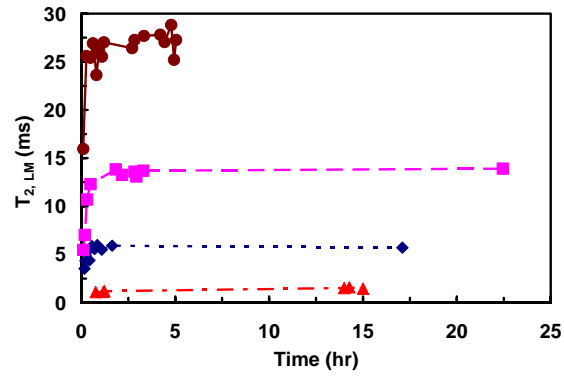
Figure 5: Time profile of $T_{2,LM}$ of the heavy crude example heated stepwise from ambient temperature to 30°C (▲), 60°C (◆), 90°C (■), and 120°C (●).