

# **INTEPRETATION OF NMR RESPONSE TO HYDROCARBONS: APPLICATION ON MISCIBLE EOR EXPERIMENTS**

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*This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Vienna, Austria, 27 August – 1 September 2017*

## **ABSTRACT**

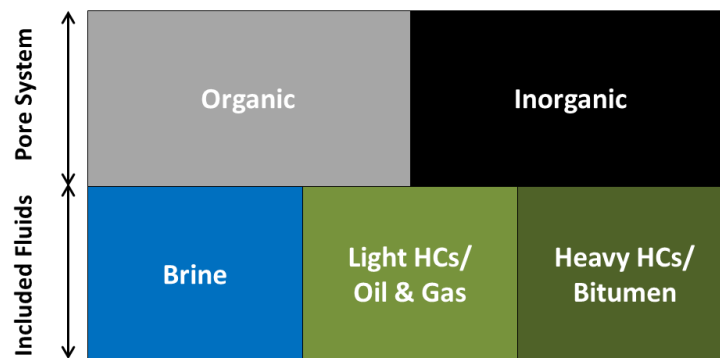
Estimation of total reserves in shale gas and shale oil reservoirs is challenging but critical. Different types of logging tools and core evaluation procedures are utilized in an attempt to address this challenge. NMR plays a vital role in understanding fluid content, rock-fluid interaction, and determination of pore body size distributions. Hydrocarbon (HC) hosting pore systems in shale include both organic and inorganic pores. Recoverable HCs include bitumen and light hydrocarbons. Their relative fractions are strongly dependent on thermal maturity. Regardless of detailed chemical characterization, ‘bitumen’ is simply defined based on mobility in this study. The apparent mobility of HCs depends on fluid composition, solubility and reservoir temperature. Historically, while verifying interpreted parameters from NMR logs (nominally 2MHz) through core measurements are done at room temperature (25-35°C). This study highlights the importance of running NMR tests at reservoir temperature. Experiments were performed for both bulk fluids and fluids within rock samples.

The results show that at a particular temperature, NMR only responds to the fraction of HCs present in the liquid phase. For routine NMR measurement, at 31°C, only the relaxation signals of compounds more volatile than C17 are acquired. Thus, the C17+ fraction would be invisible to NMR at room temperature, but perhaps not at reservoir temperature. This is critical to interpret NMR log response within the early oil and condensate windows, in which C17+ can be a major fraction. Engineers can underestimate movable HCs using routine core data as a basis for interpretation.

Based on NMR experiments for several oil samples, we observed T1-T2 distribution depends on the overall composition of total HCs and effective mobility. The results also show that in case of both light and heavy HCs, which coexist in a single phase, T1-T2 distributions for these fractions are indistinguishable. NMR parameters were used to monitor the amount, composition and effective mobility of remaining HCs after each injection and discharging cycle, during miscible EOR huff and puff experiments on Eagle Ford samples.

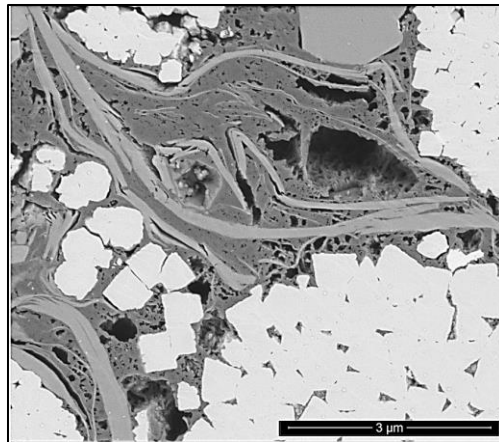
## INTRODUCTION

NMR has been proven as a useful tool to evaluate formation characteristics in both the field and the laboratory. Historically, the tool is utilized to estimate porosity, pore body size distribution, from which permeability is inferred (Coates et al. 1991[1]; Kenyon et al. 1988[2]). NMR signals, or magnetization vector are induced during the relaxation of a nuclear spin. In petroleum applications, scanning frequency is tuned to resonate with the Larmor's frequency of hydrogen at a specific magnetic field strength (Kleinberg and Jackson, 2001[3]). Hydrogen is found in water, hydrocarbons (oil and gas), bitumen, and macromolecular kerogen. NMR response to each of these components is different (Bryan et al., 2002[4] and Brown, 1961[5]) and should be evaluated. Moreover, the interaction between pore system and included fluids elevate the complication of interpreting the NMR response. **Fig.1** presents different pore systems, and included fluids which can possibly coexist in a rock formation.



**Fig. 1** General schema for different fluids and pore systems in shale. Shale is complicated by the coexistence of inorganic pores, which can be oil or water wet, and organic pores, which are generally assumed to be oil wet.

Unlike conventional rock, with a simple single inorganic pore system, with organic rich tight rocks, the interaction between fluids and void spaces are highlighted, from the pore size effect to the pore wettability effect (Yassin et al., 2016[6] and Deglint et al., 2016[7]). **Fig.2** show a fine scale SEM image of an Eagle Ford shale sample, in which pore spaces can be found among and within carbonate matrix, clay minerals, and organic matter.



**Fig. 2** Backscattered electron (SEM) image of an Eagle Ford shale sample. The image shows different pore systems, within inorganic matrix, within organic matter, or between them. The very bright features are pyrite. The darker masses are organic.

Understanding the NMR response of brine within rock sample is well established. Many previous studies, which use simple hydrocarbon components or mixtures, such as methane, dodecane (Odusina et al., 2011[8]), and isopar L (C11-C13) (Nicot et al., 2016[9]), were successful in demonstrate the presence of a dual-wettability system in organic rich shale. However, the interpretation of NMR data cannot be complete without the understanding the response from reservoir hydrocarbons (HC), which are a multi-component system. This study emphasizes the compositional and temperature effects upon the induced NMR signal from bulk HCs and HCs within the pores.

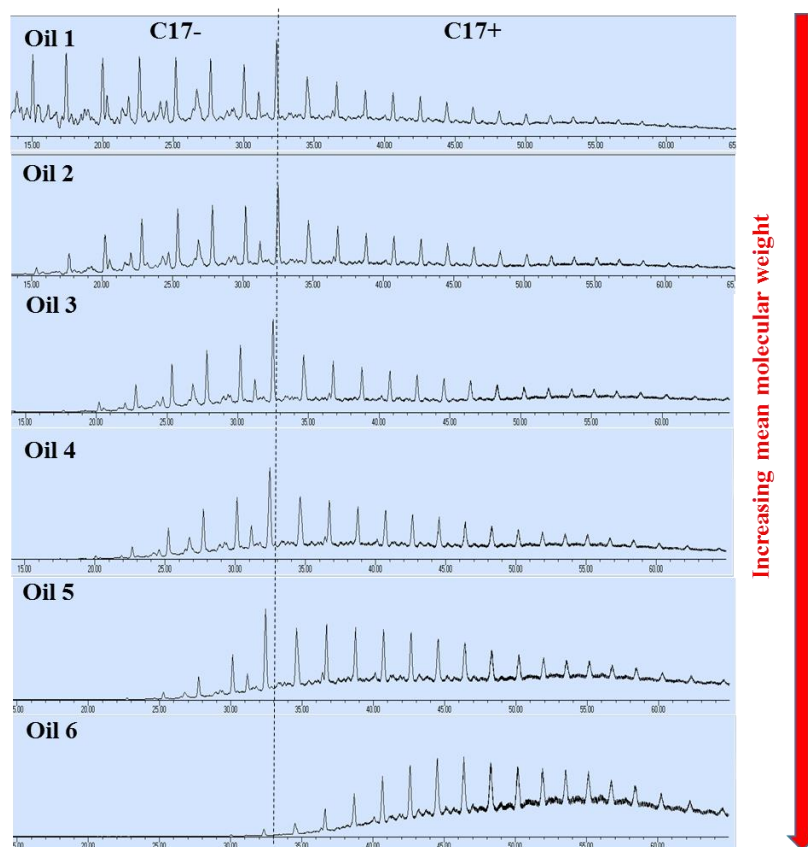
## EXPERIMENTAL INSTRUMENT & SAMPLES

HCs samples used in this study include a set of pure n-alkanes, with a carbon chain length ranging from C6 to C20. The detailed density, melting point, and vaporization temperature of these alkanes are found in Nistchem (Nistchem webbook). According to **Table.1**, C17 is the highest n-alkane occurring in the liquid phase at 31°C. A set of synthetic samples was created from the distillation of a produced crude under inert condition. Crude, or Oil 1 was heated to elevated temperatures to generate Oils 2, 3, 4, 5, and 6 with successively increasing heavy fractions of HCs. Nitrogen was continuously flowed through the heated sample container during the distillation to prevent oxidation. **Table.2** shows the detailed distillation temperatures, and sample stages at room temperature.

An Agilent™ GC-FID-MS system was used to perform compositional analyses on the set of synthetic oils. The analyses provides the detailed concentration of alkanes within each oil sample. With the benchmark as 32.5 minutes or the retention time of C17, the fraction of C17- decreases from Oil 1 to Oil 6 (see **Fig. 3**). In other words, the mean molecular weight increased respectively, which results in the reduction of mobility.

**Table. 1** Melting point, vaporization temperature and density of pure n-alkanes used in this study. Notice C17 is the highest alkane occurring in liquid phase at 31°C

Alkane	C6	C7	C9	C10	C12	C16	C17	C20
Density, g/cc	0.66	0.68	0.72	0.73	0.75	0.77	0.78	0.79
Melting Point, °C	-95	-91	-54	-30	-10	18	21	37
Boiling Point, °C	69	98	151	174	216	287	302	343

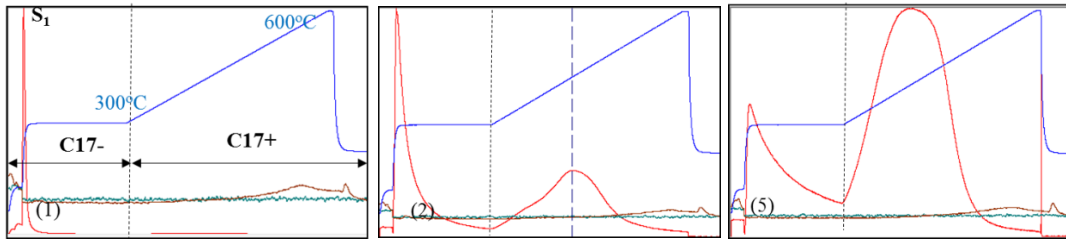


**Fig. 3** Compositional analysis, GC-FID spectra for Oil 1, 2, 3, 4, 5, 6 with retention times range from 15 to 65 minutes. With the increasing of heavy HCs fraction (C17+) corresponding to the systematic decreasing of oil mobility. C17 alkane appears at 32.5 minute (dash line).

**Table. 2** The set of synthetic oils generated from a produced crude through heating to different temperatures. At room temperature, Oil 1 and 2 occur in the liquid phase; Oil 3 appears as wax (semi-solid); and Oil 4, 5, 6 appears as solid.

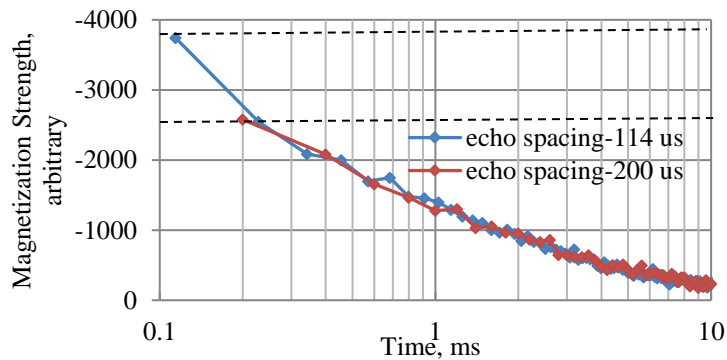
Oil ID	Crude/1	2	3	4	5	6
Distillation T, °C		100	150	200	250	300
Phase	liquid	liquid	wax	solid	solid	solid

Source Rock Analysis (SRA) or Rock-Eval® is an anhydrous pyrolysis technique, utilized to estimate parameters relating to source rock maturity and productivity level. It is also applied to measure producible HCs, from the FID response to HC components evaporated at temperature less than 300°C, i.e., the S1 peak in a pyrogram. According to **Table.1**, the producible HC measured from SRA correlated to C17- fraction. Figure.4 shows the FID pyrograms for Oil 1, 2, and 5. Respectively, S1, or C17- fraction reduces relative to C17+ fraction.



**Fig. 4** (Left to right) FID pyrograms of Oil 1, 2 and 5 (red lines.) S1 or C17- fraction includes HC components, which vaporize at temperatures (blue lines) less than 300°C. S1 or C17- reduces systematically from Oil 1 to Oil 6.

NMR spectra were acquired using two benchtop GeoSpec Oxford™ instruments with operating frequencies of 2 MHz and 12 MHz. The temperature for each instrument was set 31°C. We performed T2 relaxation and T1-T2 map measurements with an echo spacing of 114  $\mu$ s. This optimum echo spacing was chosen to capture fast relaxation components from shale samples, while prevent the interference of the fluorine signal from internal machine parts made of Teflon. **Fig.5** demonstrates the difference in acquired NMR signal as a function of echo spacing. The selection of echo spacing is extremely important while running NMR on oil prone shales, which include fast relaxation components, such as low mobility fluids or fluids in small pores (ref.)

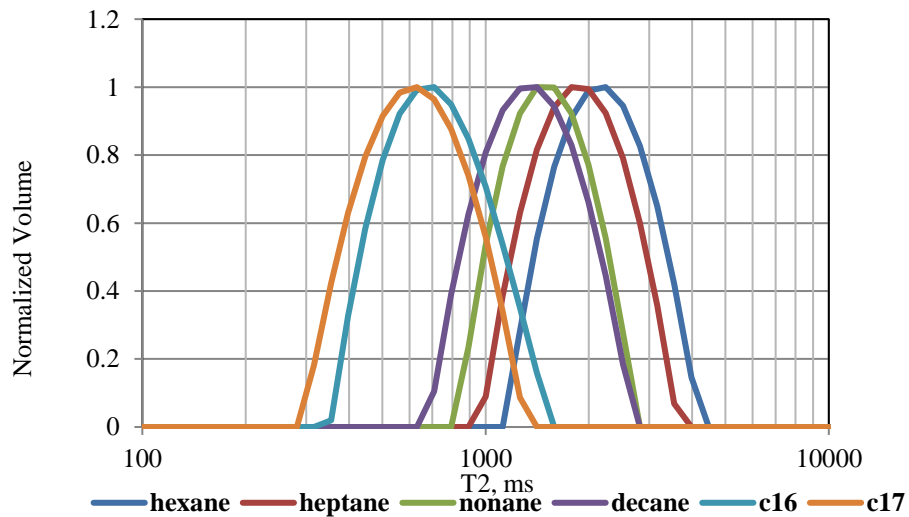


**Fig. 5** NMR data recorded on a highly viscous fluid. With smaller echo spacing, acquired signal is lower, due to the capture of signals from fast relaxation component. The total signal increase 30% in this fluid sample with echo spacing of 114 $\mu$ s.

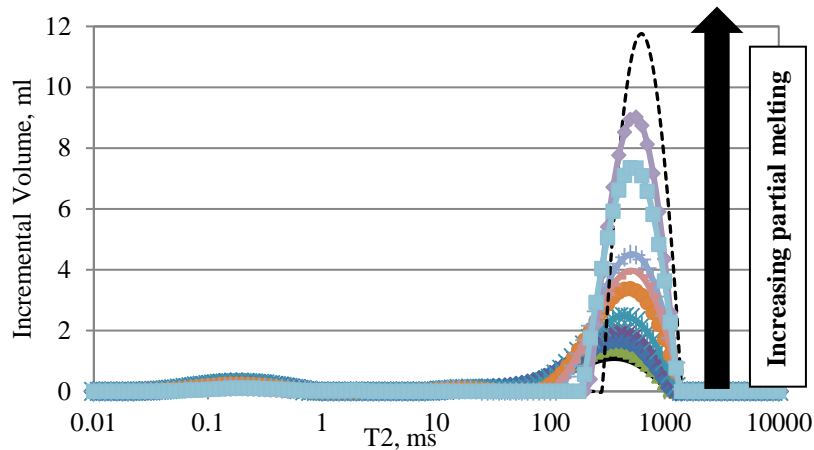
## RESULTS

Simple T2 relaxation spectra were acquired for six bulk pure n-alkanes (**Fig. 6**). The data attained by using 12 MHz NMR system, with echo spacing of 114  $\mu$ s and temperature of 31°C. The calculated log mean T2 values has a negative correlation with the length of carbon chain. This is due to the viscosity of the fluid that restricts the rotational diffusion, which makes the nuclear spin relax faster (Bloembergen, 1961[10]). However, there is no NMR signal acquired for C17 higher alkanes, which appear as solid phase at these testing conditions.

To confirm the temperature effect on NMR response of HCs, an experiment was performed on C17 alkane. First, bulk C17 was solid frozen at 4°C; then it was brought into testing condition of 31°C and NMR was continuously measured as the sample warmed. As the results of partial melting of the bulk fluid, the total amplitude increases while the  $T2_{\log \text{ mean}}$  shifts to the right (**Fig.7**.) This response indicates that temperature governs which component in a HC mixture yields a measureable NMR signal. For example, when NMR measurement was obtained on an alkane mixture at 31°C, only alkanes lower C17 response to the magnetization. On the other hand, temperature affects the liquid-solid interaction happening on the surface of the grain, which contribute to the overall relaxation rate of fluids inside pore spaces (Godefroy et al., 2001[11]). However, the focus of this study is to identify HCs components responding to NMR at a particular temperature.

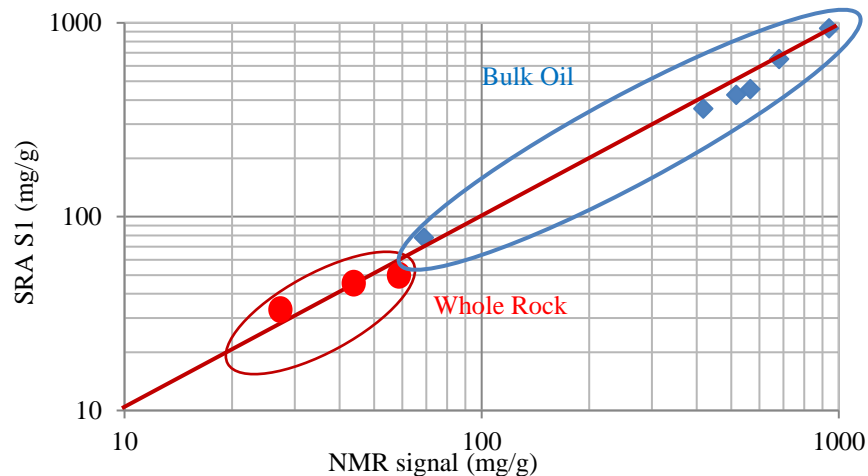


**Fig. 6** T2 distribution for different pure n-alkanes. The curves shift to the left for higher n-alkanes.  $T2_{\log \text{ mean}}$  and its inverse relation with carbon length. There is no NMR response for higher C17 n-alkanes at temperature of 31°C.



**Fig. 7** Continuous NMR response for bulk C17 alkane undergoing warming and increasing partial melting. Cumulative response increases until complete melting at 31°C (black dash line.)

NMR T1 and T2 measurements were also obtained for the set of synthetic oils, using both 2 MHz and 12 MHz instruments at 31°C. As the above results suggested, NMR response for this set of oils– Oil 1 to Oil 6– correlates well with SRA-S1 amplitude, which is sensitive to C17- or light HC fraction. The S1 signal from SRA is reported in mg/g of total HCs. Using compositional analysis for each oil samples, Hydrogen Index and mean density were estimated. These parameters are subsequently applied to convert NMR volumetric amplitudes to mg/g of total HCs. **Fig.8** shows good agreement between S1 and NMR response for the set of synthetic oils as well as HCs in some Eagle Ford shale samples.

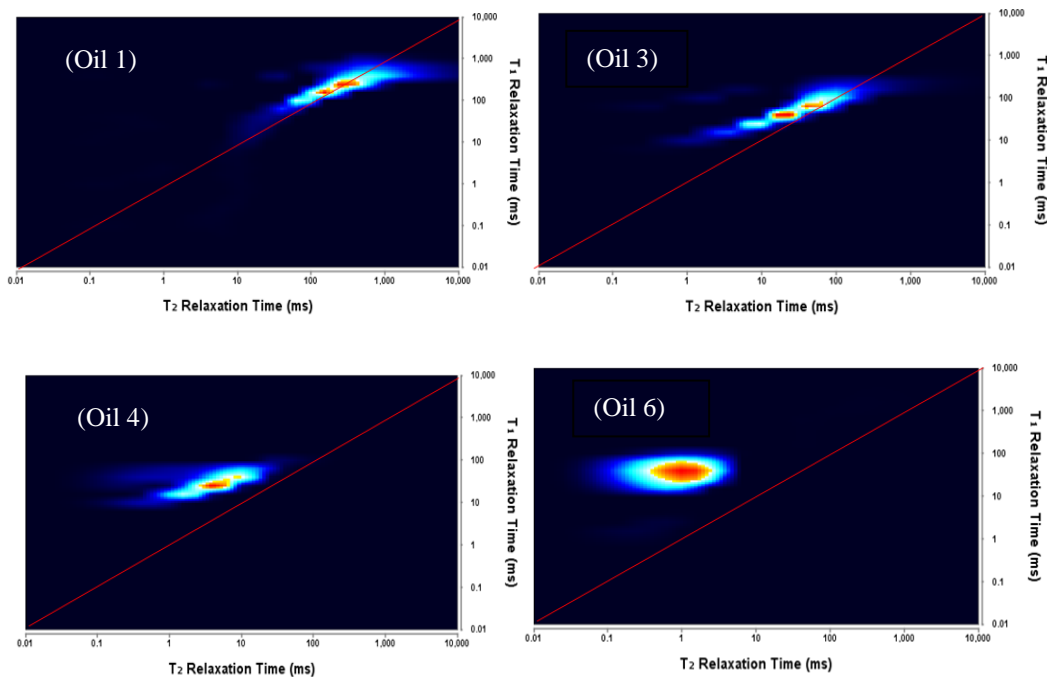


**Fig. 8** The agreement between S1, characterize for the mass of light HCs/ C17-, and NMR amplitude under the experimental temperature of 31°C.

The results suggest that at reservoir conditions, different fractions of the total HCs can be detected by NMR tools due to the tool configurations and echo times; additionally, due to

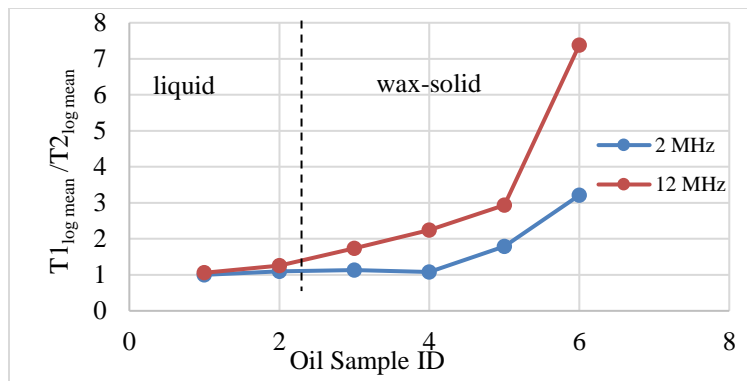
the combination fluid composition and temperature. At a specific NMR configuration, total HCs from a rock sample can be underestimated, especially with a source rock in the oil window.

Although at a specific temperature, NMR amplitude only responds to a certain HC fraction, NMR parameters, such as T1 and T2 distribution are functions of overall fluid composition. **Fig.9** shows T1-T2 maps at 12 MHz for samples Oil 1, 3, 4, and 6. With increasing viscosity or higher mean molecular weight, the signals move further from 1:1 line. **Fig.10** shows the positive relationship between T1/T2 and fluid viscosity. The separation between T1 and T2 is more pronounced in the higher frequency NMR measurement. Previous studies (Nicot et al., 2007[12]; Lo, 2000[13]) suggest using this ratio as an index for fluid mobility. With 12 MHz instrument, the clear separation between T1 and T2 can only be observed in Oil 3, 4, 5, and 6, which appear from the wax to solid form. Korb (2015)[14] presents experimental data reported in the literature (Latorraca et al., 1998[15] and Zhang, 2002[16]), which confirms the observation, that low frequency NMR is limited in differentiating the mobility of fluids. For 2 MHz measurements, the true split between T1 and T2 curves can only be observed with viscosities larger than 1000cP. However, higher operating frequency can help to estimate fluid mobility.



**Fig. 9** T1-T2 maps at 12 MHz for Oil 1, 3, 4 and 6. In all images, the red line represents 1:1 correlation between T1 and T2. The more viscous fluids show more separation between T1 and T2. Although the amplitude corresponds to C17- fraction, the distribution depends on the overall composition of a fluid.

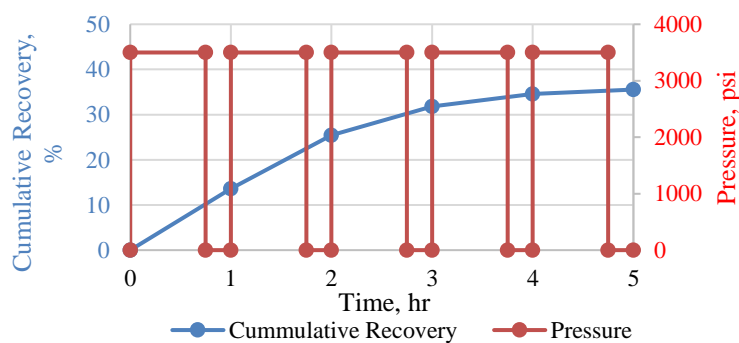




**Fig. 10** T1/T2 ratio for the set of synthetic oils. The separation between T1 and T2 is more visible for the more viscous oil, and the split is more pronounced for the higher NMR operating frequency.

## CASE STUDY APPLICATION

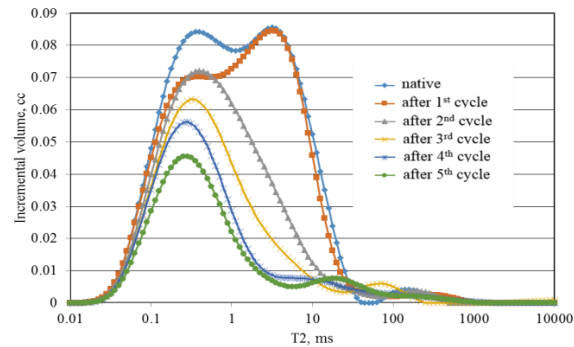
With the low price of produced crude oil and gas, economic success in newly drilled wells requires reducing cost and risk. Enhanced oil recovery is considered economically attractive for increase crude output at a marginal cost. Miscible gas injection, such as huff and puff, is the most feasible EOR method for unconventional tight reservoirs. Some preliminary field tests suggested the process could help to improve the recovery by up to 30%. The success of the project partially depends on the detection and monitoring reservoir fluid quality and quantity after each injection cycle. With an attempt to capture the change in remaining HCs through huff-and-puff, carried out a laboratory experiment to measure the NMR response from an Eagle Ford shale sample after each cycle of CO<sub>2</sub> injection; injection pressure was 3500 psi at a temperature of 170°F. The injection and production scheme is summarized in **Figure 11**.



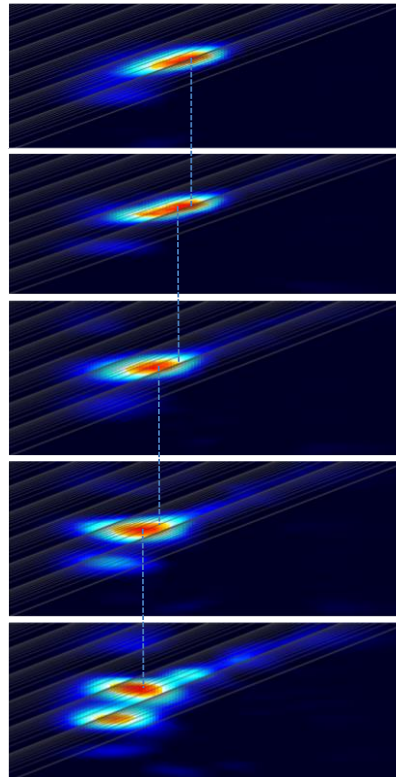
**Fig. 11** Huff and puff scheme for miscible gas injection experiment for an Eagle Ford sample. Injection pressure is 3500 psi at 170°F. Blue line represents the cumulative recovery with maximum recovery of 35%.

After each cycle, a fraction of light HCs is recovered along with the solvent gas. The T2 response helps to quantify the amount of HC that has been released after each cycle

(**Fig.12**), while the remaining fraction within the rock sample becomes heavier. T1-T2 maps provide evidence for our conclusion. In **Fig.13**, after each cycle, we observe the increasing of water signal (close to 1:1) relative to HC signal. HC signal also shifts to smaller T2, and T2 separates further from T1.

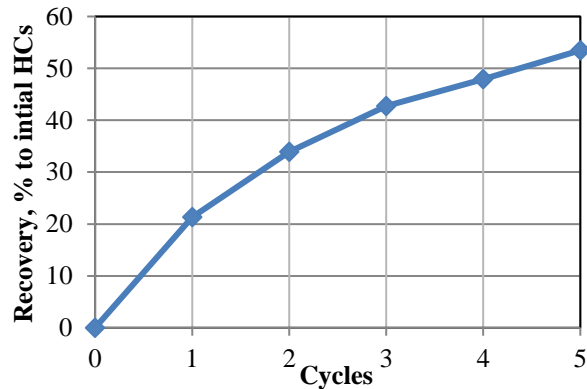


**Fig. 12** T2 distribution for the remaining fluids in the rock sample after each huff-and-puff cycle. We observe the reduction in T2 amplitude due to the recovery of light HCs from the bulk rock. Note  $T2_{\log \text{ mean}}$  shifts to the left.



**Fig. 13** T1-T2 distributions for the fluids remaining inside the rock sample after each huff-and-puff cycle. Y-axis represents T1, while x-axis represents T2; both are in scale of 0.01-10000ms. We observe the reduction in overall amplitude due to the recovery of light HCs from sample, which results in the highlight of water signal (close to 1:1). HCs signal moves further to the left. Note the color scale in each spectrum had been auto scaled.

With conventional core flooding experiment, the amount of collected fluid after each cycle is used to compute the recovery. However, with EOR experiments on tight rocks, this quantitation becomes unreliable due to the limitation of pore volume. Therefore, we propose the workflow, in which collected fluids are analyzed to understand extracted composition, while the recovery is calculated using the NMR parameters measured from the remaining HCs fraction in rock samples. With the removal of water signal (close to 1:1 line) from T1-T2 spectra, the recovery for 5 cycles of huff and puff done on an Eagle Ford sample, are plotted in **Fig.14**. Note the experiment was conducted on crushed samples with sample size from 6-8mm. Future experiments with core flooding with live monitoring using high pressure and high temperature NMR sample cell are planned.



**Fig. 14** HCs recovery after each cycle of huff and puff with CO<sub>2</sub>. The total recovery is 52%. Note the experiment was performed on crushed samples with sample size from 6-8mm.

## CONCLUSIONS

With the coexistence of HC gases, oil, bitumen, and macromolecular kerogen within a shale rock, the interpretation of NMR response has become more complicated. This study highlights the dependence of NMR response on operating configuration, HC composition and reservoir temperature. This is critical when laboratory measures are used to verify NMR log inferred parameters.

NMR only responds to the fraction of HCs present in the liquid phase. For routine NMR measurements, with temperature ranging from 25-35°C, only the relaxation signals of compounds more volatile than C17 are acquired; whereas, at the reservoir condition, relaxation signals of heavier HCs fraction can also be detected.

Although at a specific temperature, NMR amplitude only responds to a certain HC fraction, NMR parameters are functions of overall fluid composition, and NMR operating frequency. The separation between T1 and T2 is more recognizable when the apparent mobility of HC mixture decreases. Moreover, this effect is more pronounced at higher NMR frequency. From this study and literature, for NMR tool with frequency lower than 2 MHz, T1/T2 can only be used as a viscosity index when viscosity is greater than 1000 cP.

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