

Bulk saturation measurement of water and oil in porous media using ^{13}C and ^1H magnetic resonance

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Abstract. Knowledge of water saturation is essential to determine hydrocarbon-in-place during the exploration stage of petroleum reservoirs, and to monitor the sweep efficiency during the production phase. Water saturation is usually measured using three independent techniques: resistivity logging, capillary pressure saturation modeling, and a direct measurement of water in the preserved core plug samples using Dean Stark extraction. The latter requires extraction of water using hot toluene vapor, collecting this water in a graduated cylinder, and measuring the water volume. Each of these steps are error prone. This conventional method is time-consuming and involves hazardous organic solvents. This paper presents a radically different approach to measuring the water content in a porous rock sample; we exploit the presence of ^{13}C in the hydrocarbon phase. ^{13}C is a magnetic resonance (MR) active nucleus that naturally exists in hydrocarbons, but not of course in formation water. We show that water and hydrocarbon phase saturations can be derived using only two measurements: ^{13}C and ^1H MR measurements. While the ^{13}C MR measurement gives hydrocarbon content in the rock sample, ^1H MR measurement yields oil and water content. The combination of these two measurements yields water and oil saturation in the rock sample. This method was tested and validated on Bentheimer and Berea core plugs, saturated with brine and oil. Bulk saturation measurements based on ^{13}C and ^1H MR measurements were in close agreement with independent Dean-Stark saturation measurements. Results confirm that the calibrated MR signal of ^{13}C was sufficient to obtain hydrocarbon content/saturation in the porous media and it is applicable to realistic samples with complex hydrocarbon MR signals. The method requires sequential measurement of ^1H and ^{13}C in a core plug or similar sample. This may be undertaken with two MR instruments, one with a radio frequency (RF) probe tuned for ^1H , the other with an RF probe tuned for ^{13}C . Alternatively, it may be undertaken using one instrument and a doubly resonant RF probe. These measurements are greatly facilitated by a variable field MR instrument which permits sequential measurement of ^1H and ^{13}C in the same instrument with the same RF probe at the same frequency.

1 Introduction

Water saturation is a key parameter in the determination of oil- and gas-in-place. It also gives valuable information on recovery efficiency (both on displacement efficiency and volumetric sweep efficiency) in the primary, secondary, and tertiary development phases of a petroleum reservoir [1]. Industry relies on three independent techniques as standard methods for determination of water saturation. These techniques include resistivity logging [2–6], capillary pressure saturation modeling [6,7], and a direct measurement of the water content in preserved samples using the Dean-Stark distillation extraction method [8–10]. The determination of average water saturation in preserved samples requires extracting water from the samples using hot toluene

vapors, followed by collection of the extracted water. The volume of collected water is measured to obtain quantitative data on the water saturation. However, it is important to acknowledge that each of these steps is inherently prone to error. Factors such as variation in the extraction efficiency, potential losses during the collection process, and inaccuracies in volume measurement can introduce uncertainties in the final determination of water saturation. Therefore, careful attention to the experimental technique, and rigorous quality control measures, are crucial to minimize these errors and ensure reliable results [8,9]. Furthermore, this conventional method is time-consuming and involves toluene which is a hazardous organic solvent [11].

Magnetic resonance (MR) provides a robust set of techniques for investigating fluids that reside in the reservoir rock at the laboratory and wellbore scale.

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Typical MR core analysis measurement involves obtaining a distribution of transverse relaxation lifetimes, T_2 , using the well-known Carr-Purcell-Meiboom-Gill (CPMG) measurement [12,13]. In practical scenarios, when various fluids are present within the rock pore space, it is common to observe significant overlap of MR signal in the T_2 distributions of realistic samples [14–22]. This often prevents quantification of water and oil content. Early work considered the use of D_2O to obtain a signal exclusively for one of the phases [23,24]. Two-dimensional T_1 - T_2 [1,25,26] and diffusion- T_2 correlations [27,28] are alternative approaches used for signal differentiation. However, the former may still suffer from signal overlap, and the latter results in loss of fast-relaxing signal components [16]. Therefore, these measurements do not provide a general solution to the signal overlap issue for water and oil discrimination [29].

This paper introduces a novel approach to measure the water and oil content in a rock sample by employing natural abundance ^{13}C that occurs in the hydrocarbon phase. However, unlike water, hydrocarbons contain the MR sensitive nucleus ^{13}C . This characteristic allows quantification of oil content in the sample, given the absence of ^{13}C in the water phase. This provides a more reliable and quantitative approach to MR measurement that does not suffer from signal overlap. In this study, we demonstrate that water saturation and hydrocarbon saturation can be determined using ^{13}C and 1H MR measurement. The gyromagnetic ratio (γ) of ^{13}C is $\sim 1/4$ of that of 1H . Furthermore, the natural abundance of ^{13}C is $\sim 1.1\%$. This means measurement sensitivity for ^{13}C is reduced compared to 1H . However, in this paper, it is shown that a quantitative ^{13}C measurement for rock samples is still viable.

Implementation of this method involves sequential measurement of 1H and ^{13}C in a core plug or similar sample. This can be achieved with various instrument configurations. One approach is to use two different instruments, one equipped with a radio-frequency (RF) probe specifically tuned for 1H and the other instrument with an RF probe tuned for ^{13}C . Another approach is to use a single instrument with a doubly resonant RF probe. Alternatively, a variable field instrument can be utilized, which enables the sequential measurement of 1H and ^{13}C in the same instrument using the same RF probe. This configuration streamlines the measurement process and enhances the measurement efficiency. Both setups,

whether using two instruments or a variable field instrument, provide the necessary tools for conducting sequential 1H and ^{13}C measurements, which are integral to this method. In our methodology, we utilize ^{13}C measurements to acquire signals only from the hydrocarbon phase. This allows quantification of the oil phase, avoiding the aforementioned signal overlap issue. Additionally, we employ 1H measurements to obtain the bulk hydrogen content, which includes contributions from both the water and the hydrocarbon phase. A combination of the two measurements allows quantification of water and oil content in the core plug. This streamlined approach offers a simplified and efficient method for characterizing the saturations of these phases in a rock sample.

The efficacy of this method has been tested and validated on conventional reservoir samples, Bentheimer and Berea core plugs, saturated with brine and oil. The measurements of bulk saturation, derived from ^{13}C and 1H MR measurements, demonstrate a strong correlation with independent saturations obtained from the Dean-Stark extraction method. The results obtained in this study reinforce the potential for this method to replace Dean-Stark analyses.

2 Materials and Methods

Rock and fluid properties. The composition of the brine solutions is given in Table 1. Viscosity standard oils (S20, S3) [CANNON Instrument Company, PA, United States], and Decane [Thermo Fisher Scientific, US] were used as the oil phases for different samples. Bentheimer and Berea sandstone core plugs were cut and trimmed to industry-standard dimensions. The sample properties and the saturating fluids are given in Table 2.

Table 1. Salt concentration in the brine samples.

Brine ID	NaCl (g/l)	CaCl ₂ (g/l)	MgCl ₂ (g/l)	Na ₂ SO ₄ (g/l)	KCl (g/l)
Br1	101	24.1	8.2	0.75	0.52
Br2	20	-	-	-	-

Table 2. Sample properties.

Core #	Fluids	Formation	Length (cm)	Diameter (cm)	Dry mass (g)	Saturated mass (g)	Pore volume (ml)	Porosity (%)	Preparation method
BH1	Br2, S20	Bentheimer	5.16	3.80	115.0	128.7	13.6	23.2	Flooding
BH2	Br2, Decane	Bentheimer	5.16	3.80	114.6	128.8	14.0	23.9	Flooding
BH3	Br1, S20	Bentheimer	5.15	3.79	115.3	127.6	13.9	23.8	Flooding
BA1	Br2, S20	Berea	5.28	3.79	125.4	137.4	11.9	19.9	Flooding
BA2	Br1, decane	Berea	5.14	3.79	122.8	135.1	11.3	19.4	Centrifuge
BA3	Br2, Decane	Berea	5.14	3.79	121.7	133.5	11.6	20.0	Flooding

MR instruments. ^{13}C measurements were acquired using a variable field magnet (MR Solutions, Guildford, Surrey, UK) at 3.1 T which corresponds to a resonance frequency of 33.7 MHz for ^{13}C . The RF probe was a homemade birdcage. The magnet is permanently connected to a magnet power supply (Cryomagnetics, Inc., TN, US). GIT system software (Green Imaging Technologies, Inc., NB, Canada) was employed to execute CPMG measurements.

^1H MR measurements were undertaken at two magnetic fields. 33.7 MHz ^1H MR measurements were performed on the variable field magnet at 0.79 T. All hardware used for these measurements was the same as that used for ^{13}C measurements, and only the magnetic field was changed. ^1H measurements were also undertaken using a Maran DRX-HF (Oxford Instruments Ltd, Oxford, UK) 0.2 T permanent magnet which has a resonance frequency of 8.5 MHz for ^1H . The RF probe was a custom-built solenoid, 4.4 cm inner diameter, driven by a 1 kW 3445 RF amplifier (TOMCO Technologies, Sydney, Australia).

MR measurements. ^{13}C and ^1H CPMG MR experiments were undertaken to determine the ^{13}C and ^1H signals. The acquisition parameters used to perform CPMG measurements are given in Table 3.

Data Processing. To obtain the MR signal intensity, the CPMG decay was fitted to single, biexponential or multiexponential decay function shown in Eq. 1. Taking $t = 0$ gave the back-extrapolated signal at time zero.

$$S(t) = \sum_i S_i \cdot \exp\left(\frac{-t}{T_2^i}\right) \quad (1)$$

where $S(t)$ is the CPMG signal as a function of time, t .

Figure 1 is a flowchart illustrating the procedure used to obtain the oil and water volume in the core plugs based on ^{13}C and ^1H MR data. First, a ^{13}C measurement was performed. Given the absence of ^{13}C in the water phase, this signal unambiguously originates from the oil which can be used to calculate quantitative oil volume, V_o . The signal intensity from ^{13}C measurement was converted to oil volume using a reference sample by having its signal/volume. Having gravimetric data on dry and one phase saturated states of samples, the pore volume, PV , of the rock was calculated. Finally, the volume of water in the core sample can then be calculated ($V_w = PV - V_o$). In the general case of gravimetric data not being available, V_w can be measured using a combination of ^{13}C and ^1H MR CPMG measurements of the target sample (total signal from core plug saturated with oil and water) as well as ^1H MR CPMG on reference samples of oil and brine. The volume of water can be calculated by having the total ^1H signal, and oil volume and having signal/ volume of reference samples of the oil and water, following Eq. 2:

$$\begin{aligned} & ^1\text{H signal}_{\text{sample}} \\ &= V_o \times \left(\frac{{}^1\text{H signal}_{\text{reference}}}{\text{volume}_{\text{reference}}} \right)_{\text{oil}} \\ &+ V_w \times \left(\frac{{}^1\text{H signal}_{\text{reference}}}{\text{volume}_{\text{reference}}} \right)_{\text{brine}} \end{aligned} \quad (2)$$

Application of an appropriate reference sample eliminates problems arising from ^{13}C natural abundance. If we have a reference sample for oil, there is no need to know the ^{13}C natural abundance and carbon density. In the case of brine, an appropriate reference sample also eliminated the need to know the hydrogen density. This simplifies the calculations.

Ultimately, the water volume obtained using MR measurement was compared with that measured using the Dean-Stark method to examine the accuracy of this procedure.

Table 3. Parameters used for each instrument.

Experiment/ Parameter	Variable field magnet (33.7 MHz)		^1H (8.5 MHz magnet)	
	^{13}C	^1H	Brine	oil
Instrument				
90° pulse duration (µs)	42.3	9.2	10.3	
180° pulse duration (µs)	85.9	19.7	20.5	
Frequency (MHz)	33.7	33.7	8.6	
CPMG				
Relaxation delay (sec)	25	15	10	5
Echo time (ms)	1		2	1
Number of echoes collected	1000		2000	
Number of points collected at each echo	9		9	
Number of scans	32	16	32	
Dwell time (µs)	5		8	

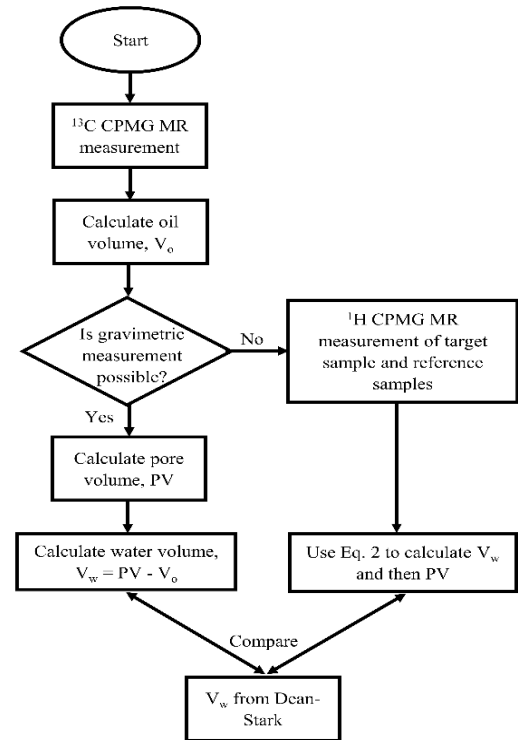


Fig. 1. Flowchart of the water saturation determination.

Raw data and sample calculation. Figures 2-3 show a typical T_2 distribution and T_2 decay of the ^{13}C signal at 33.7 MHz based on CPMG data for sample BH1. ^{13}C T_2 relaxation is governed by molecular dynamics and environment. Figure 4 show T_2 distribution of the ^{13}C signal at 8.5 MHz based on CPMG data for sample BH1.

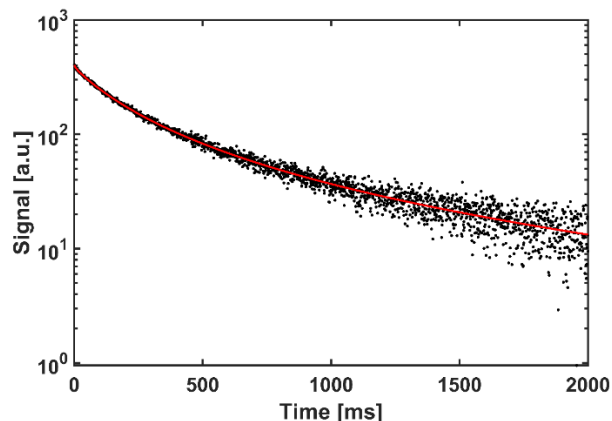


Fig. 2. Signal decay for ^{13}C CPMG of core plug BH1. 2048 echoes were collected.

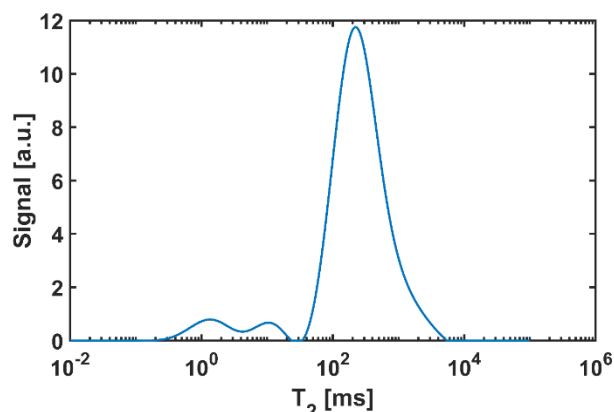


Fig. 3. ^{13}C T_2 distribution of core plug BH1.

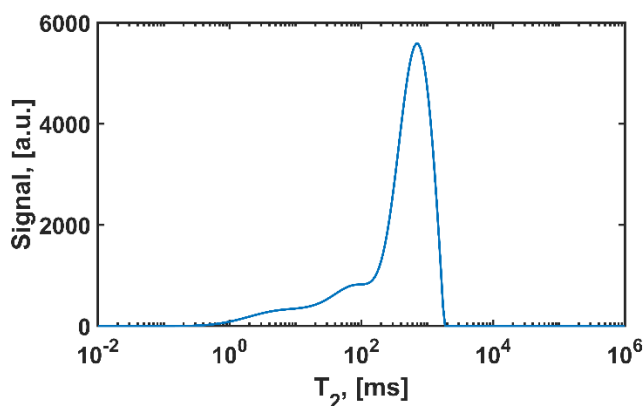


Fig. 4. ^1H T_2 distribution of core plug BH1.

The MR signal and volume of the reference samples are outlined in Table 4. The signal intensities reported in this table are in arbitrary units. Therefore, the signal intensities should not be directly compared.

The back extrapolated signal of ^{13}C MR measurement divided by the reference sample's signal per volume directly yields the oil volume in ml. To obtain the water volume, Eq.2 was used which yields water volume in ml.

Table 4. Reference samples ^{13}C and ^1H signal to volume ratio.

Reference sample	^1H Signal / Volume 33.7 MHz	^1H Signal / Volume 8.5 MHz	^{13}C Signal / Volume 33.7 MHz
Oil (Decane)	427	10800 ¹	26.8 ²
Brine (Br2)	414	10050	-

¹Different instruments have different signal arbitrary units (a.u.).

²As a less sensitive nucleus, the ^{13}C measurement yields a lesser signal than ^1H .

3 Results and Discussion

Table 5 shows the results based on the approach described in the flowchart of Figure 1. The first column is the sample ID which corresponds to the samples summarized in Table 2. The second column is the calculated oil volume based on ^{13}C measurements and the procedure for analysis is described in the material and methods section. The third column is the water volume calculated with Eq. 2 at 33.7 MHz for ^1H . The fourth column is the water volume calculated with Eq. 2 at 8.5 MHz for ^1H . The fifth column is the volume of water obtained by conventional Dean-Stark measurement. The sixth column is the pore volume based on 33 MHz ^1H data which is the summation of oil volume obtained by ^{13}C measurements and water volume calculated in column 3. The seventh column is the pore volume based on 8.5 MHz ^1H data which is the summation of oil volume obtained by ^{13}C measurements and water volume calculated in column 4. The eighth column is the gravimetric pore volume, and the ninth column is the water saturation obtained by subtracting oil volume (by ^{13}C) from gravimetric pore volume. The last column is the water saturation calculated based on Dean-Stark measurement and gravimetric pore volume data.

The results show there is good agreement between the water saturation obtained by ^{13}C and ^1H MR measurements and industry standard Dean-Stark measurements.

Figures 5-7 show the correlation between the water saturation calculated by MR measurement and the Dean-Stark method. In the Dean-Stark experiment water volume is measured directly. To convert water volume to water saturation, PV of the Gravimetric data is used for Dean-Stark based water saturation in Figures 5 -7. Also, in these figures the oil volume is obtained by ^{13}C (33.7 MHz) MR measurement. Figure 5 shows the correlation between the water saturation obtained by combination of ^{13}C (33.7 MHz) MR measurement and Gravimetric data. In this case, the pore volume is obtained by Gravimetric data. So, water volume (V_w) is calculated by ($V_w = PV - V_o$) and then water saturation is calculated by V_w/PV . Figure 6 shows the correlation between the water saturation obtained by combination of ^{13}C (33.7 MHz) and ^1H (8.5 MHz) MR measurements. In this case the pore volume and water volume are calculated based on the approach described in section Materials and Methods. In

Table 5. Results of saturation measurements with MR and Dean-Stark.

Core #	V _o from ¹³ C [ml]	V _w ¹ H 33 MHz [ml]	V _w ¹ H 8.5 MHz [ml]	V _w , D.S. [ml]	P.V. from 33 MHz [ml]	P.V. from 8.5 MHz [ml]	P.V. gravimetric [ml]	Sw from ¹³ C and ¹ H 33.7 MHz [%]	Sw from ¹³ C and ¹ H 8.5 MHz [%]	Sw only from ¹³ C and gravimetric [%]	Sw from D.S. [%]
BH1	10.7	-	3.23	2.5	-	13.9	13.6	-	23.2	21.2	18.4
BH3	6.8	-	-	7.4	-	-	13.9	-	-	51.0	53.6
BA1	7.4	-	5.0	4.3	-	12.4	11.9	-	40.3	37.8	36.5
BA2	6.4	-	4.1	4.5	-	10.5	11.2	-	39.0	43.1	39.9
BA3	6.3	5.0	5.3	5.0	11.3	11.6	11.6	44	45.7	45.7	43.1
BH2	7.5	6.1	6.3	6.2	13.6	13.8	14.0	45	46.0	46.0	44.3

this case water saturation is calculated by dividing water volume to the MR driven PV. Figure 7 shows the correlation between the water saturation obtained by combination of ¹³C (33.7 MHz) and ¹H (33.7 MHz) MR measurements. The other procedures for this case are the same as the previous case in Figure 6.

We observed that the water saturation obtained by Dean-Stark experiments was typically lower than the water saturation obtained by MR measurements in most of our samples. The errors in the Dean-Stark experiment typically result in loss of water and therefore lower water saturation. By contrast, the short lifetimes of the ¹³C CPMG MR measurement result in a lower oil volume, and a higher water saturation.

It should be noted that the Dean-Stark measurement requires many hours or days while the MR data can be undertaken in 1-3 hours. In the Dean-Stark experiment the sample is not preserved while the MR experiment is non-invasive and non-destructive. Azeotropic distillation in the Dean-Stark method requires toluene which is a toxic fluid. In the Dean-Stark method there is a risk of losing the water and toluene vapors from the connections. Also, attachment of the water droplets to the condenser or other connections can cause errors in the final water volume. These can be prevented by properly cleaning the apparatus and using the vacuum seal in connections, however human error inevitably leads to inaccuracies. On the other hand, ¹³C and ¹H measurements require good control on the parameters affecting the signal. The repetition time, number of scans, digital filter setting, tuning and matching of the probe and all other parameters should be checked before acquisition of the data and they should be consistent between the reference sample and the

target samples. If the fluids occupying the pore space have dominant short components that can not be detected based on the echo time in the CPMG method, then the error of the MR method may be reduced by using free induction decays. MR determined saturations have uncertainties that are calculated based on the propagation of uncertainties that originate with the basic MR measurements.

We have tested our saturation determination technique by ¹H and ¹³C MR measurements on conventional reservoir samples. There are two main possibilities for unconventional reservoir samples. The first case is shale samples. This case has been studied with ¹H MR measurements in several studies [30–33]. In the above referenced works, pore volume and fluid saturation were determined for unconventional samples using ¹H MR measurements. They used the relaxation properties of the fluids to distinguish solid matter and exclude its MR signal in calculation of pore volume. Bitumen was quantified based on its relaxation time signature. We, however, are using ¹³C measurement to directly detect MR signal from oil. Assuming different relaxation times for the less mobile species, ¹³C MR relaxation measurements might distinguish short lifetimes and long lifetimes which can assist in a similar fashion to ¹H measurements as described by the papers mentioned above to calculate the organic matter and bitumen content. The benefit of using ¹³C MR measurement is direct detection of organic matter without interference from the water phase. (2) In the case of a non-shale bitumen containing sample, a ¹³C measurement on a dry sample may help determine the residual bitumen content of the sample. The method proposed in this paper calculates the

total ^{13}C containing hydrocarbons. Therefore, comparing the ^{13}C signal on a saturated sample and a dry sample can separate the residual bitumen from the total oil content.

We used ^{13}C and ^1H measurements for the first time for measuring water and oil saturation, as well as to demonstrate the possibility of replacing Dean-Stark measurements with ^{13}C and ^1H MR measurements. The authors do not claim that our methodology is the best answer for all cases, however employing different techniques, approaches, and pulse sequences can extend the application of ^{13}C MR measurements in porous media and make it a routine analysis in commercial labs especially for complex systems when current methods are not suitable.

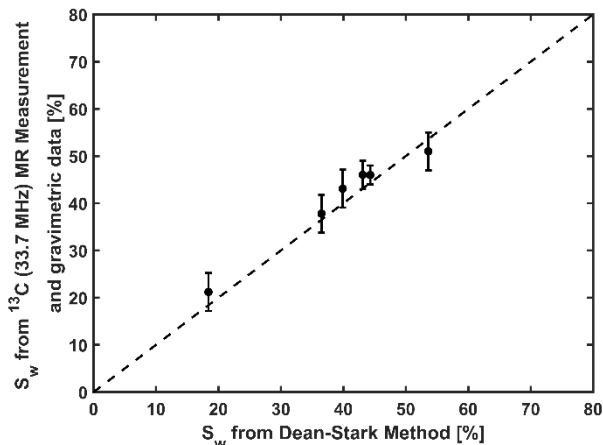


Fig. 5. Correlation between water saturation obtained by ^{13}C MR-Gravimetric (column 11 in Table 5) and Dean-Stark (column 12 in Table 5).

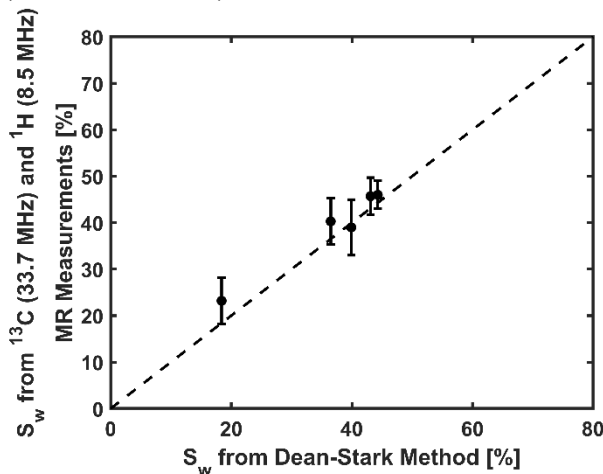


Fig. 6. Correlation between water saturation obtained by ^{13}C (33.7 MHz) and ^1H (8.5 MHz) (column 10 in Table 5) and Dean-Stark (column 12 in Table 5).

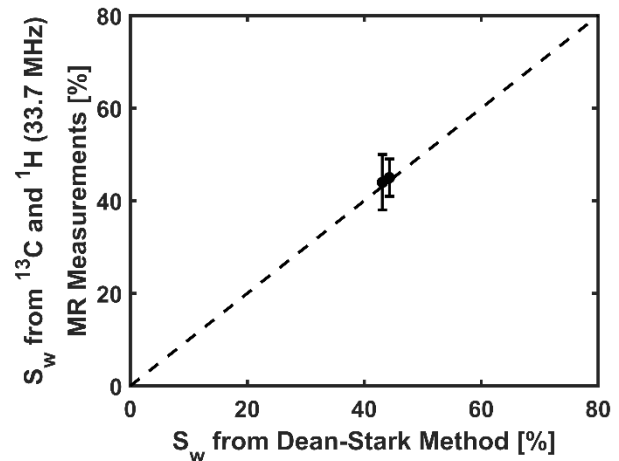


Fig. 7. Correlation between water saturation obtained by ^{13}C (33.7 MHz) and ^1H (33.7 MHz) (column 9 in Table 5) and Dean-Stark.

4 Conclusion

The saturation of fluids within porous media is a fundamental and critical parameter in petroleum engineering. While ^1H MR has demonstrated accurate saturation measurements for well controlled model systems, applying the ^1H MR procedure to real samples is often complex and, in many cases, impractical. As a result, magnetic resonance has garnered less attention for saturation determination. Industry-standard methods can often be time-consuming and prone to errors. These methods, while widely employed, involve complex procedures, significant sample preparation and sample handling, data collection, and analysis which can contribute to increased time requirements and potential inaccuracies.

This study utilized ^{13}C measurements to determine the oil saturation within Berea and Bentheimer sandstone core plugs. To validate the accuracy of the ^{13}C results, ^1H MR measurements were combined with the ^{13}C data to calculate the water and pore volume within the core plugs. Subsequently, the volumes of oil and water obtained through MR were compared with those obtained using the industry-standard Dean-Stark method. This comparison allowed for an assessment of the agreement between MR-based measurements and the well-established Dean-Stark method to quantify the oil and water content of the core plugs.

The results obtained provide confirmation that water saturation can be accurately determined using ^{13}C and ^1H MR measurements, with acceptable errors ($\pm 3\%$) [9]. In order to further minimize this error for conventional core plugs, certain adjustments can be made. One approach is to reduce the echo time, which helps to mitigate the impact of short lifetime components in the measurements. Additionally, increasing the signal-to-noise ratio of the CPMG method can enhance the accuracy of the measurements especially for ^{13}C measurements.

Part of the error observed in the Dean-Stark measurements is attributed to the preservation of the samples. This error is minimized in commercial labs by

implementing special core handling procedures that ensure optimal preservation conditions.

Another source of error stems from the Dean-Stark apparatus used for comparison. To minimize this error, it is crucial to thoroughly clean the apparatus before each experiment and employ vacuum sealing to prevent any leaks from the joints. Furthermore, optimizing the duration of the experiment is important to ensure complete removal of water from the core plug, particularly from smaller pores. By implementing these measures, the overall error in the determination of water saturation can be significantly reduced, leading to more precise and reliable results in practical applications.

In this paper, our findings demonstrate that utilizing ^{13}C MR measurements permits accurate determination of the volume of oil in a given sample. However, to measure the volume of water, additional information such as gravimetric data or ^1H MR measurements are required to quantify the water volume as well as the pore volume.

We used a variable field instrument for ^1H and ^{13}C measurements. Although this instrument is convenient as it allows for the utilization of a single instrument and a single RF probe, streamlining the experimental setup and reducing complexity, it is not widely available. We have established that ^1H and ^{13}C MR data can be acquired with two different MR instruments. In our case, one was set to 8.5 MHz for ^1H and the other instrument was set to 33.7 MHz for ^{13}C measurements. It would also be possible to have an instrument at one field, but with two different RF probes tuned for different nuclei.

The utilization of a variable field magnet offers the potential added advantage of obtaining ^{23}Na MR data in addition to ^{13}C and ^1H MR measurements. By combining these three data sets, it should be possible to measure the salinity, specifically the sodium content, of the brine within the core plug. This is particularly relevant in the context of smart water injection experiments. Future work will focus on exploring the measurement of brine salinity using combined MR information from ^{13}C , ^1H , and ^{23}Na data.

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