

Investigation of temperature characteristics of secondary organic matter and hydrocarbons in the early Jurassic Marrat formation using laboratory NMR techniques

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Abstract. Understanding physical properties of secondary organic matter and hydrocarbons in terms of their mobility with temperatures and production potential is crucial for initial assessment of oil and gas reservoirs. In this study laboratory NMR techniques are utilized to investigate carbonate reservoir samples from two wells in the Early Jurassic Marrat formation, Kuwait. The core samples are dolomite with secondary organic matter or bitumen, primarily insoluble pyrobitumen which partly occludes the primary inter-crystalline porosity. Samples are in forms of chunk pieces or crushed to the GRI sizes and measured at various temperatures from ambient to reservoir temperature of 130°C. NMR 1-D T2 relaxation time and 2-D T1-T2 map measurements were performed at 2MHz (LF) for the purpose of comparing to NMR well logging, and at 23MHz (HF) for higher sensitivity and better map resolutions, respectively. The HF measurements with an inter-echo spacing time TE=0.07 ms show that a solid-like component with its T2<0.1 ms can be detected at the ambient temperature. On the other hand, the LF maps or T2 distributions failed to detect such solid-like components due to the longer inter-echo spacing time (TE=0.2 ms) used in the measurements but the LF signals are enhanced at the elevated temperatures indicating the contributions from the mobilized solid-like components. In order to interpret NMR logging, a further data analysis method was applied to the LF NMR T2 distributions at various temperatures by fitting the T2 spectra into a summation of three Gaussian functions. The results suggest that the two longer T2 components are temperature dependent following the Arrhenius relationship, while the shortest T2 component is temperature independent in the temperature range studied. To our best knowledge, it is the first time that both LF and HF laboratory NMR techniques are used to study solid organics or bitumen in carbonate rock samples. The techniques will be extended to combining core cleaning processes in searching for effective cleaning methods.

1 Introduction

Understanding the properties of secondary organic matter is crucial for the accurate interpretation of rock core samples. Bitumen and pyrobitumen can act as a binding material, cementing grains together and reducing porosity and permeability within the rock. This can have a significant impact on fluid flow properties, affecting the reservoir potential and the efficiency of oil extraction techniques. Additionally, the presence of secondary organic matter can also introduce artifacts and contamination during core analysis, influencing the efficacy of rock core cleaning methods and procedures, potentially leading to inaccurate measurements and interpretations.

The Early Jurassic Marrat Formation, located in various regions around the world, including the Middle East, is renowned for its significant hydrocarbon reservoir potential. However, the presence of secondary organic matter, such as bitumen or pyrobitumen, can complicate the analysis and interpretation of rock core analysis from this formation.

Considering these challenges, rock core cleaning methods and procedures need to be tailored specifically to account for the unique properties and behaviors of secondary organic matter. Conventional cleaning techniques, such as solvent extraction and acid treatment, may not effectively remove or dissolve bitumen or pyrobitumen, leading to incomplete cleaning and compromised core analysis.

Nuclear Magnetic Resonance (NMR) techniques are widely utilized in the study of bitumen and pyrobitumen due

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to their ability to provide valuable insights into physical and chemical properties of these organic materials. The asphaltene content in crude oil samples was determined by NMR spectroscopy techniques [1]. NMR relaxometry provides insights into the dynamics and mobility of bitumen and pyrobitumen molecules, leading to gaining information about the molecular interactions, viscosity, and rheological properties of these organic materials [2].

In this study laboratory NMR relaxometry techniques are utilized to investigate carbonate reservoir samples from two wells in the Early Jurassic Marrat formation, Kuwait. Results from both higher frequency (HF), 23 MHz, and lower frequency (LF), 2 MHz, measurements at various temperatures from ambient to reservoir temperature of 130°C suggest that the two longer T2 components in the core samples are temperature dependent following the Arrhenius relationship, while the shortest T2 component is temperature independent in the temperature range studied. This study will be extended to combining core cleaning processes in searching for effective cleaning methods.

2 Experimental

2.1 Core samples

The core samples in forms of chunk pieces or core plugs are taken from two wells in the Early Jurassic Marrat formation, north Kuwait. They are located on an attached carbonate back-stepping shelf to ramp system that developed in the Early Jurassic in an arid to semiarid climate. The core plugs are dolomite with organic matter or bitumen, primarily insoluble pyrobitumen which partly occludes the primary inter-crystalline porosity. The origin of this pyrobitumen is still somewhat uncertainty but the most likely explanation involves mixing of an early gas charge and later oil charge. Samples are labelled as SA and RA from two different depths.

2.2 Nuclear Magnetic Resonance (NMR)

NMR measurements were performed at nominal 2 MHz (Lower Frequency, or LF) on an Oxford MARAN analyzer, and at 23 MHz (Higher Frequency, or HF) on a MR Cores analyzer. Both instruments are equipped with a variable temperature NMR core holder so that samples can be measured at different temperatures. The LF (2 MHz) T₂ measurements were carried out using the standard CPMG (Carr–Purcell–Meiboom–Gill) sequence with an inter-echo spacing time of 200 μs. The HF NMR measurements were made with a 50 mm diameter probe so that intact core or chunk samples up to 1.5 inches in diameter can be analyzed. The T₂ data were encoded using a CPMG sequence with an echo spacing of TE = 0.07 ms. The T₁ data were encoded

using an inversion recovery sequence. The T₁-T₂ correlation data were acquired using a pulse sequence of combining T₁ and T₂ data acquisitions, where 64 T₁ wait steps were used and 2500 echoes with TE=0.07 ms were recorded at each T₁ wait step, then processed using an Optimized Truncated Singular Value Decomposition (OTSVD) inversion method [3] to obtain the 2D T₁-T₂ map of 121 by 121 bins. A standard sample of a known amount of water mixed with D₂O sealed in a glass vial was used to calibrate the NMR instrument for quantitative data acquisition.

3 Results and Discussion

For its higher sensitivity and better map resolutions, the HF NMR measurements were performed on the samples with a total acquisition time of 16 minutes. Figure 1 shows the 23 MHz T₁-T₂ maps of the two samples at ambient temperature. The circled region with T₂ < 0.1 ms is attributed to solid organic materials in the sample. The top right signal region is due to mobile hydrocarbons in pores. The maps indicate that the porosities of the two samples are very much different, 3.9 PU (porosity unit) for the SA and 9.6 PU for the RA, respectively.

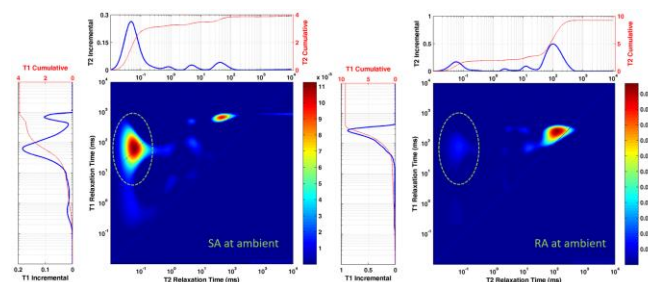


Fig. 1. 23 MHz T₁-T₂ maps of sample SA (left) and sample RA (right) at ambient temperature. The circled region with T₂ < 0.1 ms is attributed to solid organic materials.

For the purpose of interpreting NMR logging data to evaluate effects of the organic matters such as bitumen, it is necessary to perform lower frequency measurements. However, the same 2-D measurements at 2 MHz would need at least 16 hours for the data acquisition because of the lower sensitivity and longer inter-echo spacing time so that the majority of the NMR signals from the shortest T₂ component would be missed, leading to a much lower signal to noise ratio (SNR). We will therefore focus on 1-D T₂ measurements. As showing in Figure 2, where the short T₂ peak is at approximately 0.5 ms because most of the solid-like signals (T₂ < 0.1 ms) at ambient conditions is not detectable in the LF measurements with TE = 0.2 ms. Comparing to the HF data, the short T₂ peak contains contributions from the solid-like organic materials, most likely bitumen, in the rock.

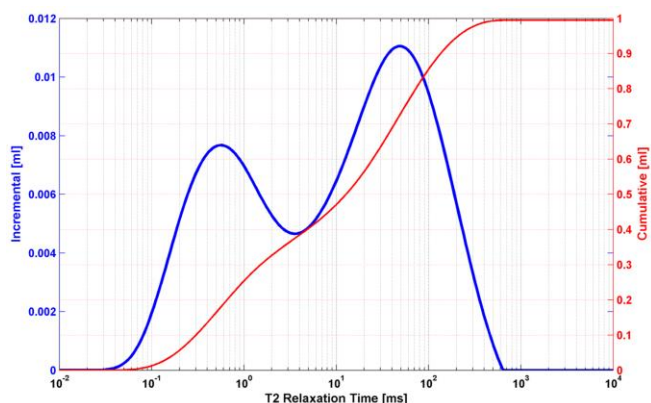


Fig. 2. T2 distribution of the sample SA measured at ambient conditions at 2 MHz with TE=0.2ms.

Viscosities of bitumen and other hydrocarbons are strongly temperature dependent [4]. If the solid-like organic materials in the rock samples consist of bitumen or pyrobitumen, the NMR T2 should be temperature dependent.

The SA sample was measured at various temperatures to obtain its T2 distributions from ambient temperature to 135°C (275°F). No pressure was applied. Temperature correction of the NMR volumes are performed according to the Boltzmann distribution. The T2 distributions are shown in Figure 3. It is clearly seen that the amplitude of the short T2 component has increased significant at elevated temperatures, suggesting the solid-like organic matters in the sample are mobilized to become detectable by the LF NMR measurements.

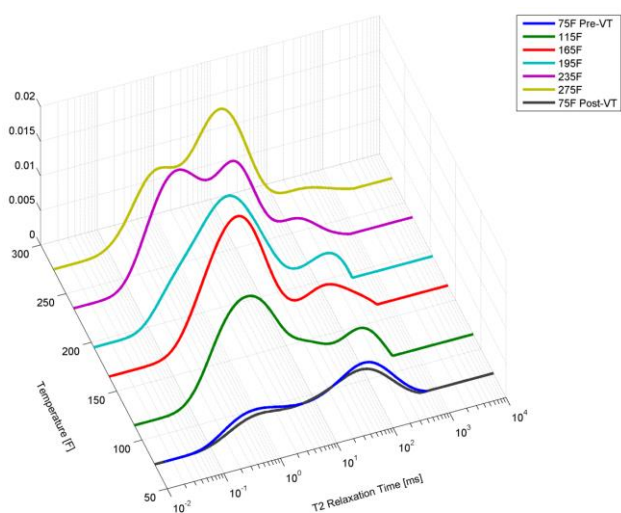


Fig. 3. 2MHz NMR T2 distributions of the sample SA at various temperatures from ambient to 135°C (275°F).

According to the famous Bloembergen-Purcell-Pound (BPP) theory, the NMR transverse relaxation time T2 can be expressed as below [5,6]:

$$\frac{1}{T_2} = C \left[3\tau_c + \frac{5\tau_c}{1+\omega_0^2\tau_c^2} + \frac{2\tau_c}{1+4\omega_0^2\tau_c^2} \right] \quad (1)$$

Where C is a constant of molecular structure, τ_c is the molecular correlation time, which is the measure of molecular mobility, ω_0 is the Larmor frequency. For the rock core cases, and for the temperature range studied, $\omega_0\tau_c \ll 1$, it then leads to $1/T_2$ is proportional to τ_c . Combining with the Arrhenius relationship, the equation (1) can be expressed as:

$$\frac{1}{T_2} \propto \tau_c = \tau_0 e^{-\left(\frac{E_a}{RT}\right)} \quad (2)$$

where E_a is activation energy in kcal/mol, T is the sample temperature in Kelvin and R is the universal gas constant, 1.987×10^{-3} kcal K⁻¹ mol⁻¹.

The equation can be re-arranged as:

$$\ln(T_2) = \left(\frac{E_a}{RT}\right) - C \quad (3)$$

C is a constant. As it can be seen, $\ln(T_2)$ is inversely proportional to temperature. A plot of $\ln(T_2)$ vs $1/T$ reveals a linear relationship, and the activation energy E_a can be derived from the slope of the line.

A further data analysis method was applied to the LF NMR T2 distributions of the SA sample at various temperatures by fitting the T2 spectra to a superposition of Gaussian distributions. In our case, the T2 spectra were fitted into a summation of three Gaussian functions to obtain T2 values, i.e. peak positions, and amplitudes of peaks. For its simplicity, we assigned a fixed T2 value of 0.54 ms to the shortest T2 peak, which may be associated with a solid-like organic matter in the sample.

Each T2 distribution was fitted to three Gaussian functions with a fixed T2 value for the first left i.e. the shortest T2, component, which appears at the temperature of 74°C and its amplitude reaches to the maximum at 113°C then reduces at higher temperatures, as shown in Figure 4. The middle peak (blue curve) is attributed to bitumen in the sample, and the longest T2 peak is thought to be oil in pores, possibly unconnected pores.

The results suggest that the two longer T2 components are temperature dependent following the Arrhenius relationship equation (2), while the shortest T2 component is temperature independent in the temperature range studied,

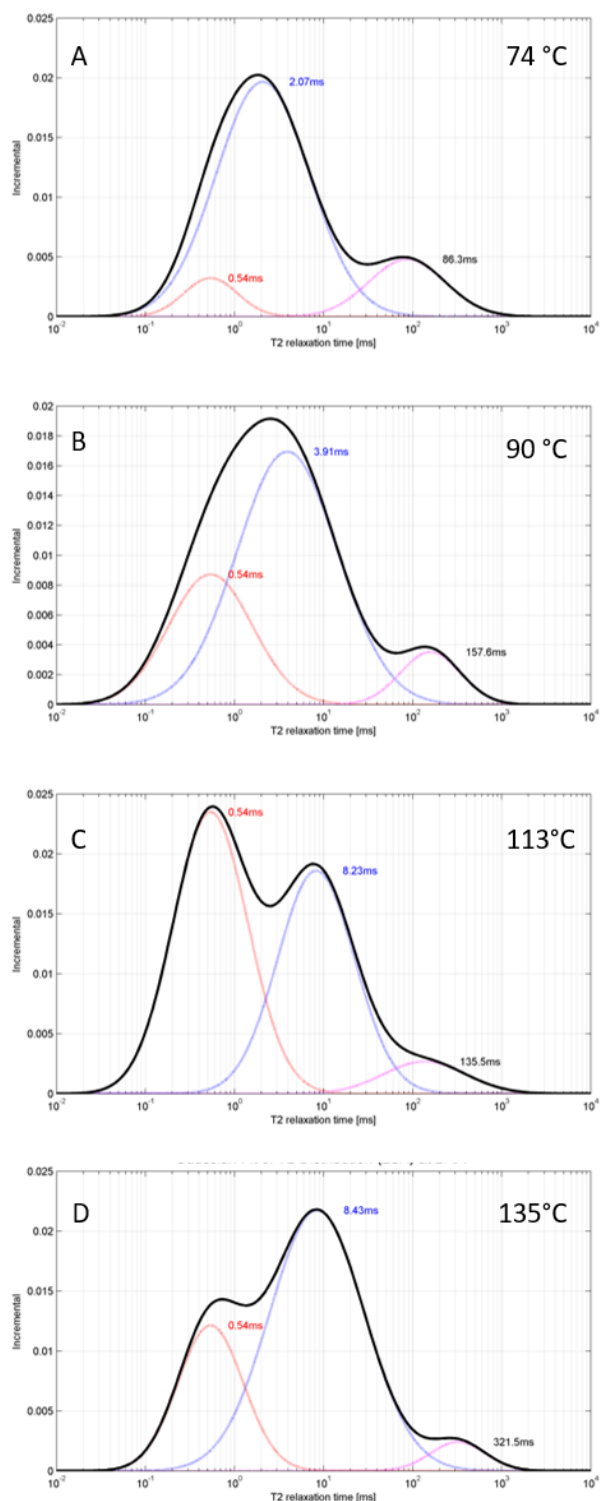


Fig. 4. T2 distributions of the SA sample at selected temperatures of 74, 90, 113, 135°C, respectively.

The T2 of bitumen and T2 of oil in the sample as a function of the sample temperature are plotted in the Figure 5. They both fit into linear lines with slopes of 3.2269 and 1.953, respectively, in turn, leading to the activation energies of 6.412 kcal/mol for bitumen, and 3.881 kcal/mol for the pore oil in the sample.

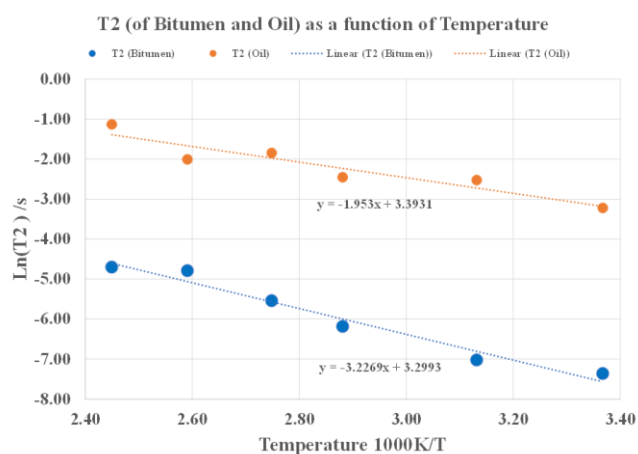


Fig. 5. T2 of bitumen and Oil as a function of the sample temperature from ambient to 135°C.

4 Conclusions

NMR 1-D T2 relaxation time measurements were performed at 2MHz (LF) at various temperatures for the purposes of understanding behavior of bitumen and comparing to NMR well logging. The 23 MHz (HF) measurements with an inter-echo spacing time $TE=0.07$ ms show that a solid-like component with its $T_2 < 0.1$ ms can be detected at the ambient temperature. On the other hand, the LF maps or T2 distributions failed to detect such solid-like components due to the longer inter-echo spacing time ($TE=0.2$ ms) used in the measurements but the LF signals are enhanced at the elevated temperatures indicating the contributions from the mobilized solid-like components, i.e. bitumen. The T2 of the bitumen is correlated with the sample temperatures following the Arrhenius equation. To our best knowledge, it is the first time that both LF and HF laboratory NMR techniques are used to study solid organics or bitumen in carbonate rock samples. The techniques will be extended to combining core cleaning processes in searching for effective cleaning methods.

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