High Temperature Fast Field Cycling Study of Crude Oil

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Abstract

A set of crude oil samples with different composition and characteristics is studied by means of Fast Field Cycling (FFC) ^{1}H relaxometry, which probes the distribution of longitudinal relaxation times T_1 as a function of the Larmor frequency. Investigation of T_1 profiles at different temperatures is able to provide an insight into the dynamics and structural changes of oil components, with our particular interest being the high temperature behaviour of asphaltene. It is well-known that asphaltenes tend to form porous clusters in crude oils, which can cause severe problems for the process of oil extraction. Therefore, FFC experiments are conducted on Stelar Spinmaster FFC2000 in the temperature range 203K < T <443K, where the upper limit of 443K is aimed at approximating the typical maximal in-situ well temperatures. FFC relaxometry data of crude oils at such a high temperature are obtained for the first time with the use of a specially modified NMR probe. Inverse Laplace transformation is applied to the longitudinal magnetization decays, yielding T_1 distributions at different frequencies. A comparative analysis of these distributions for different Larmor frequencies and temperatures showed that there is a systematic variation of the frequency dependence of T_1 correlating with the asphaltene content in the samples, at temperatures similar to the well conditions.

Keywords

Fast Field Cycling, Nuclear Magnetic Resonance, Crude Oil, Asphaltene, Inverse Laplace Transformation.

1. Introduction

Nuclear magnetic resonance (NMR) has been widely used to study crude oils both in bulk and in reservoirs [1-6]. Among other NMR methods, Fast Field Cycling (FFC) relaxometry [7] is of particular interest for the laboratory research of oils, since it provides an opportunity to obtain information about the oil composition and molecular dynamics, from the distribution of longitudinal relaxation times T_1 as a function of Larmor frequency. Creating conditions similar to those existing downhole, e.g. pressure, temperature, etc., allows one to predict the behaviour of the aforementioned oil characteristics in the borehole. This information helps to significantly improve the efficiency of oil extraction and transportation.

The focus of this research is set on investigating the effect of presence of asphaltene molecules in crude oils on the T_1 relaxation time distribution at the high temperatures experienced downhole. This problem is of special interest since the influence of even small amounts of asphaltene on the rheological properties of oil is significant because of the tendency of these molecules to form porous aggregates. The mechanism of asphaltene aggregation is not completely understood, and several models describing this process can be found in the literature [5,6]. Even though a number of techniques and methods have been employed to monitor the formation of large aggregates in oils [8], each have their own shortcomings, necessitating further methodological developments in this area. In this paper FFC relaxometry is used to investigate the crude oil's temperature behavior with a particular focus on the high temperatures (up to ∽443K), corresponding to the higher end of in-situ well temperature. However, conventional FFC probes are not designed for use at such temperatures. Therefore, the prediction of the features of the T_1 distributions at that temperature has been made based solely on theoretical modeling and extrapolations from laboratory measurements. In this work a specially designed and constructed high-temperature probe for use in a Stelar Spinmaster FFC2000 relaxometer, is employed to fulfill the goal of obtaining crude oil's longitudinal relaxation characteristics at in-situ well temperatures.

2. Samples and experimental methods

Crude oil samples with known SARA (saturate, aromatic, resin, asphaltene) composition analysis (Table 1) are used for the study. Oil 24 is a so-called waxy oil consisting predominantly of saturated organic compounds and it contains no asphaltenes as well as Oil 10, which allows the use of these two samples as reference ones while comparing with asphaltene-containing Oils 5, 16 and 11.

Oil	Saturates,%	Aromatics,%	Resins,%	Asphaltenes,%	Viscosity,cp (303K)
24	96.2	3.7	0.1	0	-
10	67.1	24.9	7.9	0	5.91
5	52.1	27.2	16.1	4.9	14.1
16	53.4	22.8	17.7	6.6	969.4
11	37.9	32.4	18.3	12.9	61.45

Table 1. SARA (saturate, aromatic, resin, asphaltene) composition analysis for 5 different types of crude oils and viscosities of 4 of them.

Longitudinal magnetization relaxation decays are measured on a Stelar Spinmaster FFC2000 relaxometer (Stelar s.r.l., Mede, Italy), covering Larmor frequencies in the range 0.01 MHz $< f <$ 25 MHz at temperatures 203K $< T <$ 443K (with different limits depending on the sample). All the samples have been subjected to differential scanning calorimetry experiments first, and showed no phase transitions at temperatures from 293K down to 203K. The abovementioned high-temperature homemade probe is used for FFC measurements. It takes advantage of placing the radiofrequency NMR coil outside of a vacuumed dewar, thus, separating the heated sample from the sensitive part of the NMR circuit, see figure 1. As is well known, crude oils are a complex mixture of different molecules with a broad range of sizes, shapes and properties, resulting in complex molecular dynamics. Consequently, their NMR response cannot be described by a single relaxation time, and the resulting distribution of T_1 is obtained using a fast inverse Laplace transform (ILT) [4].

Figure 1. The high-temperature NMR probe used for the FFC measurements on Stelar Spinmaster FFC2000 relaxometer

3. Results and discussion

In Figure 2 T_1 distributions for 5 crude oil samples obtained with use of the ILT algorithm are presented. Smoothing parameter and time limits are kept the same in order to allow a direct comparison of the results. It is seen that the waxy Oil 24 behaves as a simple liquid, showing no signs of dispersion at any of the temperatures, whereas the other 4 samples demonstrate a clear dispersion of the average relaxation time at lower temperatures, along with a narrowing of the distributions at higher Larmor frequencies. Interestingly, Oils 24, 10 and 5 experience almost no dispersion of T_1 at the highest temperature, reaching the values of the same order of ∽1s, which is a sign of the extreme narrowing regime ($\omega_0 \tau_c \ll 1$). However, Oil 16 and Oil 11, having the largest asphaltene content of 6.6% and 12.9% respectively, are not found to be in the extreme narrowing regime at the temperature T=443K. This implies that there are low-mobility components (possibly associated with asphaltene) in these samples, which are effectively contributing to the NMR relaxation even at the highest measured temperature. Moreover, high-temperature T_1 spectra of Oil 11 yield two peaks: a well-pronounced long-time one and a smaller short time one, showing dispersion even at the highest temperature. The analogous short-time peaks at the highest temperatures for Oil 5 and 16 are attributed to the spurious noise effects due to their inconsistency observed in the stack plots. This finding is promising and it is now being followed up by a more detailed experimental study, implying transverse NMR relaxation and T_1-T_2 correlation measurements.

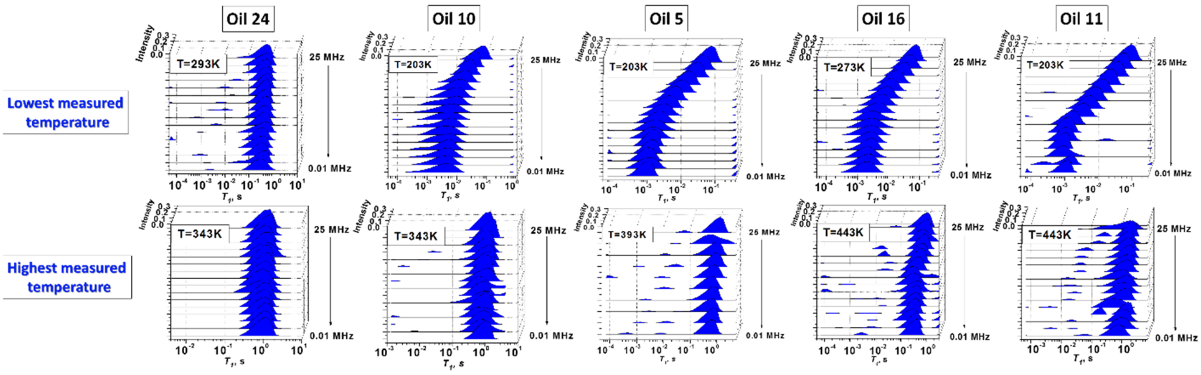

Figure 2. Longitudinal NMR relaxation times T_1 distributions for 5 crude oil samples obtained with use of inverse Laplace transformation algorithm.

4. Conclusions

Field-cycling relaxometry study of crude oils at the high temperatures experienced under in-situ conditions (~443K) is performed for the first time. Longitudinal relaxation curves are analyzed with use of the inverse Laplace transformation algorithm to obtain the spin lattice relaxation distributions. It is shown that oils with a significant asphaltene content possess T_1 Larmor frequency dispersions even at the highest measured temperatures, reflecting a direct sensitivity to the asphaltene content and dynamics. In addition, the relaxation time distribution of the oil with the highest asphaltene content (12.9%) shows the second short-time peak, which can also be attributed to the presence of asphaltene. We plan to conduct further NMR experiments to quantify the effects, to build a model for describing the high-temperature behavior of asphaltene in crude oils.

References

[1] S. Stapf, A. Ordikhani-Seyedlar, N. Ryan, C. Mattea, R. Kausik, D. E.Freed, M. D. Hürlimann, Energy & Fuels 28 (4) (2014) 2395–2401.
[2] S. Stapf, A. Ordikhani-Seyedlar, C. Mattea, R. Kausik, D. E. Freed, Y. Q. Song, M. D. Hürlimann, Microporous and Mesoporous Materials 205 (2015) 56–60.
[3] J. J. Chen, M. D. Hürlimann, J. Paulsen, D. E. Freed, S. Mandal, Y. Q. Song,ChemPhysChem 13 (2014) 2676–2681.
[4] D. E. Freed, M. D. Hurlimann, Comptes Rendus Physique 11(2) (2010) 181–191.
[5] L. Zielinski, M. D. Hürlimann, Energy and Fuels 25 (11)(2011) 5090–5099.
[6] L. Zielinski, I. Saha, D. E. Freed, M. D. Hurlimann, Y. Liu, Langmuir 26 (7) (2010) 5014–5021.
[7] R. Kimmich, E. Anoardo, Progress in Nuclear Magnetic Resonance Spectroscopy 44 (2004) 257-320.
[8] O. C. Mullins, E. Y. Sheu, A. Hammami, A. G. Marshall, Eds. Asphaltenes, Heavy Oils, and Petroleomics; Springer, 2007.