



¹H NMR spectroscopy and low-field relaxometry for predicting viscosity and API gravity of Brazilian crude oils – A comparative study



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HIGHLIGHTS

- ¹H NMR spectra and relaxation times of 76 crude oil samples were measured.
- PLSR models for viscosity and density prediction were developed.
- Regression model from relaxation data delivered a superior performance.
- Spectra and relaxation data were merged and new models were developed.
- A synergistic effect between these NMR responses was reported.

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ABSTRACT

¹H NMR spectra and transversal relaxation time (T_2) distributions of 76 Brazilian crude oil samples, ranging from light to extra-heavy, were measured and compared by Hierarchical Clustering Analysis (HCA) and Principal Component Analysis (PCA). Partial Least Squares Regression (PLSR) models were developed to predict crude oil viscosity and density in terms of the American Petroleum Institute (API) gravities derived from their individual NMR responses. Relaxation-based models delivered better predictive performances for both viscosity and API, with a standard error of prediction (SEP) of 0.220 log cP and 1.027 °API. In addition, the synergistic effect between the two distinct NMR responses was evaluated for the first time by merging spectra and relaxation data into a single PLSR model. This hybrid spectra-relaxation model delivered superior performance compared to stand-alone models, with an SEP of 0.186 log cP and 0.811 °API.

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1. Introduction

In the petroleum industry, from upstream activities to downstream activities, viscosity and density are two of the most important physico-chemical properties of crude oils. In oil exploration, the spatial variation of these properties must be accurately mapped for proper reserve assessment, well placement, reservoir simulation and well-test interpretation [1,2]. In a processing context, it is important to understand these properties to define the performance of the crude that refineries use for blending operations [3,4]. Thus, it would be useful to develop new methods to accurately characterize viscosity and density in a time- and cost-efficient way.

In several papers, the potential of spectroscopy, chromatography and mass spectrometry-based technologies, such as Infrared Spectroscopy (IR) [5], Gas Chromatography (GC) [6], High

Performance Liquid Chromatography (HPLC) [7] and Mass Spectrometry (MS) [8], have been explored as alternative methods for crude oil and petroleum-based product characterization. However, since the discovery of Nuclear Magnetic Resonance (NMR) [9,10], NMR-based technology has attracted special attention from the oil industry, mainly because (i) it is a rapid, non-destructive and non-contact method, (ii) it is particularly robust for industrial and field applications, and (iii) it can be used to analyze dark and opaque samples, such as crude oil, with little or no extra preparation. An excellent review of NMR methods can be found in Silva et al. [11].

For on-line and in situ petroleum characterization, the NMR technology used in industry varies according to the application context. The first, most common technique for oil refineries consists of measuring the ¹H NMR spectra of the incoming crude oil feedstock using on-line mid-resolution NMR spectrometers. A multivariate controller estimates the physico-chemical properties of each incoming feedstock based on the ¹H NMR spectra and determines the relative amounts of each constituent required to

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deliver a near constant blended crude supply [12]. These analyzers operate with magnetic field strengths around $B_0 \sim 1.5$ Tesla, corresponding to a Larmor frequency of $\nu_0 \sim 60$ MHz for ^1H .

The second NMR technology is used in the context of well logging and consists of measuring the ^1H NMR relaxation times from oil-bearing formations using downhole low-field NMR relaxometers. In current NMR logging tools, it is not possible to obtain high resolution spectra because their highly heterogeneous and low magnetic field strengths, typically ranging from 3.75 to 50×10^{-3} Tesla, corresponding to ν_0 values from 150 kHz to 2 MHz for ^1H . In basic wireline NMR logging operations, the sensor continuously performs relaxation measurements while being moved along the borehole [13]. At each depth, the raw relaxation curves are numerically inverted to produce relaxation time distributions. Rock and fluid properties are modeled directly from these distributions, as is done for the NMR spectra.

There have been several scientific papers reporting the development of spectral [14,15] or relaxation [16,17] models for predicting crude oil properties, but none of them compares the predictive performances of the two NMR approaches. In addition, to the best of our knowledge, no research has been carried out to evaluate the potential of combining both ^1H NMR spectroscopy and low-field relaxometry responses into a single model. This hybrid approach is particularly relevant when NMR spectral characterization of petroleum became available down-hole. The growing NMR research on hardware miniaturization [18] and on high-resolution spectroscopy from grossly heterogeneous magnetic fields [19,20] suggest that chemical-shift based well logging tools may be commercially available in the near future.

The purpose of this paper is two-fold. First, the individual ^1H NMR spectroscopy and low-field relaxometry responses in crude oils were studied through the means of exploratory data analysis tools and compare the resulting multivariate model performances for the prediction of viscosity and density in terms of degrees of American Petroleum Institute (API) gravity. Second, a ^1H NMR spectroscopy-relaxometry hybrid model for these two crude oil properties was developed and the predictive accuracy of the hybrid model with stand-alone models was compared.

2. Experimental section

2.1. Sample selection and characterization

The dynamic viscosity and density of 76 crude oil samples from different Brazilian reservoirs were characterized according to ASTM D7042 [21] in a Stabinger SVM 3000 Generation 2 viscometer (Anton Paar, Austria). Samples were kept sealed in their original flasks and stored in a refrigerator before characterization and NMR measurements. All samples were provided by Petróleo Brasileiro SA (PETROBRAS).

2.2. ^1H NMR spectroscopy

2.2.1. Sample preparation

Without any previous treatment, a small amount (equivalent to one drop) of neat crude oil was transferred from the original flask into a 5-mm precision NMR tube. Then, $\text{CDCl}_3 + 0.1\%$ TMS was added to the NMR tube to a height of 5.5 cm height (which extended well beyond the sensitive area of the receiver coil), and the mass concentration (w/w) was calculated.

2.2.2. Data acquisition

We did not have access to a mid-resolution 1.5 Tesla process NMR analyzer; therefore, quantitative ^1H NMR spectroscopy measurements were performed on an 11.75 Tesla Varian VNMR5

(Varian, USA) spectrometer equipped with a 5 mm direct detection double channel ^1H - $^{19}\text{F}\{^{15}\text{N}-^{31}\text{P}\}$ Pulsed Field Gradient (PFG) probe. Applying a single 90° pulse of $10 \mu\text{s}$, ^1H NMR spectra at 35.0°C with 65 K points over a spectral width of 12 ppm was recorded. Sixteen successive acquisitions, spaced by a recycle delay of 60 s, were averaged to improve the signal to noise ratio.

2.2.3. Data processing

After manual phasing and baseline correction, all ^1H NMR spectra were normalized by concentration. To obtain a more representative sample of mid-resolution process NMR data [35] to allow for a fair comparison with the low-field relaxometry data, the spectra recorded at 500 MHz were automatically discretized into $m = 12$ spectral bins, as shown in Table 1, according to the spectral region definitions proposed by Molina et al. [22].

2.3. ^1H NMR low-field relaxometry

2.3.1. Sample preparation

Crude oil samples were thermalized in an electric oven for 4 h and were then transferred directly into the NMR equipment in their original sealed flasks.

2.3.2. Data acquisition

^1H NMR transversal relaxation times (T_2) were measured on a 0.047 Tesla Maran Ultra-2 (Oxford Instruments, UK) relaxometer equipped with a 52 mm single ^1H channel PFG probe. Using a standard Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence, T_2 relaxation curves were recorded at 35.0°C using 8192 echoes and an inter echo-time of $\tau_e = 400 \mu\text{s}$. Thirty-two successive acquisitions, with a recycle delay of 30 s, were averaged to improve the signal to noise ratio.

2.3.3. Data processing

The relaxation distributions $f(T_2)$ were obtained by inverting the CPMG data with the following equation: $\frac{I(t)}{I(0)} = \int_{-\infty}^{\infty} \exp\{-\frac{t}{T_2}\} f(T_2) d(T_2) + \varepsilon$, where $I(t)$ is the amplitude of the echo and ε is the noise. The inversions were performed by using the program 2D Laplace Inversion ver. 2 (Magritek, New Zealand) and running an NNLS (non-negative least squares) algorithm with Tikhonov regularization [23,24]. The final distributions were computed with $n = 128$ relaxation bins, logarithmically distributed between 0.1 ms and 10 s.

2.4. Multivariate data analysis

Hierarchical Clustering Analysis (HCA) and Principal Component Analysis (PCA) were applied to the ^1H NMR spectra and relaxation data to reveal the underlying dataset structure, making it possible to identify similarities between samples and to detect potential outliers. Partial Least Squares Regression (PLSR) was subsequently used to build predictive models for viscosity and API from the crude oil NMR responses. In addition to normalization by concentration, receiver gain, and number of scans, the NMR data was mean centered (i.e. the column means were subtracted from every variable before analysis) before the multivariate data analyses.

All analyses were performed by using The Unscrambler-X ver.10.3 (Camo, Norway) and selecting the Euclidian distance measure with the complete linkage clustering method for HCA. The non-linear iterative partial least squares (NIPALS) [25] algorithm was used for both PCA and PLSR. These multivariate techniques are widely used in research and industrial applications, and only a brief description will be presented in the next section. Detailed explanations of the multivariate methods can be found in classical textbooks [26–28].

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