

Comparison of viscosity data from Brazilian crude oils using NMR

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Oil is a very complex multi-component system constituted by tens of thousands of different hydrocarbon molecules, and its ¹H NMR relaxation profile can be modeled as a linear combination of characteristic relaxation times from the measurable hydrogens present in their structure. [1, 2]. This work presents a study of different Brazilian crude oils (A, B and C) with attempt to explore the benefits of a multivariate data analysis (MVA) approach in the viscosity prediction of crude oils using nuclear magnetic resonance spectroscopy (NMR) data [3].

The ¹H spectra were run in 5 % solutions of a 1:1 (v/v) CDCl₃:C₂Cl₄ mixture at 300 MHz using 45° pulses, 1.0s intervals between pulses and 128 transients were accumulated. The ¹³C NMR, experiments were performed on a Varian INOVA 500 MHz spectrometer equipped with 5 mm probe (bbsw) at 25°C (298K). NMR samples were prepared in CDCl₃ (600µL) with sample concentration of ~100 mg. The ¹H transverse relaxation time, T₂, measurements were performed in duplicate at 45°C in a 460 Gauss (2MHz for 1H) bench-top NMR spectrometer MaranUltra (Oxford Instruments, UK), using a 52 mm probe equipped with a homemade variable temperature device. ¹H NMR relaxometry was used because it is a non-destructive method and requires a very little sample and it is quickly.

The °API classification of oils A, B and C is 13,3, 18,5 and 19,9, respectively. Results of the spectroscopic signals of ¹H and ¹³C NMR are summarized in Table 1. The samples showed lower values of H_{ar} and higher proportions of aromatic carbon (C_{ar}), suggesting that ring systems contain aromatic hydrocarbons with high degree of substitution by alkyl groups. Comparing samples (A, B and C), oil A presents the highest proportion of aromatic carbon than oils B and C, which indicates its higher degree of polyaromatics. Oil C has a lower proportion of C_{ar} and substituted alkyl groups, indicating a lower proportion of aromatic rings. The measurement of transverse relaxation time (T₂) obtained by low field NMR technique showed that B and C presented similar ranges of relaxation time (100 µs < T₂ < 100 ms, characteristic of medium/heavy oils), and oil A showed a relaxation profile with a shift to the left (100 µs < T₂ < 6ms, characteristic of heavy /extra heavy oils) (Fig.1). Analysis of the Apparent Hydrogen Index (HIA) shows that, A presented a deficit in HIA while B and C showed a very similar value that decreased in number of detectable hydrogen atoms per unit mass of oil (Table 2). Thus there is an interesting correlation between relaxometry data and

¹H and ¹³C chemical shifts, both in agreement with relative viscosity.

FIGURES

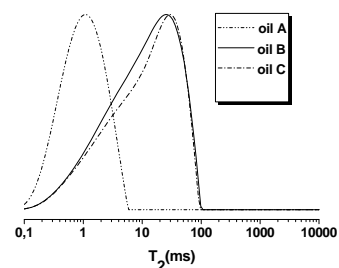


Fig. 1. Relaxation times (T₂) of the oils: A, B and C.

TABLES

Table 1
Regions of chemical shift of ¹H NMR and ¹³C NMR

NMR	Chemical Shift (ppm)	Integrated Area (%)		
		A	B	C
¹ H	0 – 4	91.86	92.77	95.28
	6.0 – 9.0	8.14	7.23	4.72
¹³ C	0-70	85.68	88.81	92.68
	110 – 170	14.32	11.19	7.32

Table 2

Apparent Hydrogen Index (HIA) of the samples

Sample	HIA
A	0.503
B	0.953
C	0.957

References

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