

Study of crude and plasma-treated heavy oil by low- and high-field ^1H NMR

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Low-field ^1H NMR experiments are routinely employed in many petroleum-related applications, including indirect evaluations of oil viscosity, petrophysical analysis of porous rocks, etc [1]. Usually the low-field NMR analyses of oils involve the measurement of transverse (T_2) and/or longitudinal (T_1) relaxation times, hydrogen index and diffusion coefficients. In this work, ^1H low-field NMR experiments were combined with thermogravimetry (TG), rheological measurements and ^1H high-field NMR in order to assess the physical and chemical changes occurring in a heavy crude oil submitted to treatments in a plasma reactor.

The starting material used was a heavy crude oil with an API gravity of 10.1. This material was treated in a double dielectric barrier (DDB) plasma reactor, using different plasma gases: natural gas (NG), CO_2 or H_2 , with reaction times of 1, 1.5 and 4h, respectively [2]. The rheological properties were measured in an Anton Paar rheometer at 70°C . The TG curves were recorded on a Shimadzu TGA-50 thermobalance, from room temperature up to 900°C . The low-field ^1H NMR experiments were conducted in a MARAN Ultra spectrometer, from Oxford Instruments, at 27.5°C . The T_1 and T_2 measurements were performed using the inversion-recovery method and the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence, respectively [1]. The T_1 and T_2 distribution curves were computed by the inverse Laplace transform (ILT) of the time-domain signals, using the WinDXP® software. ^1H high-field NMR experiments were performed in a Varian INOVA NMR spectrometer, operating at 400 MHz. The NMR spectra were produced by Fourier transform (FT) of the time domain signal, after a single pulse excitation experiment.

The results of rheological analysis showed a reduction in the viscosity of the plasma treated oils, when compared to the crude oil. The lowest viscosity was found for the sample prepared with the CO_2 plasma. TG data indicated a significant drop in the water content for all plasma-treated samples, following the same trend observed for the viscosity reduction. These facts suggest that the water loss occurring during the plasma treatments is a key factor determining the reduction in the viscosity of the oil-water mixture.

Whereas the TG and rheological measurements give information on the overall behavior of the oil-water mixture, the use of ^1H low-field NMR relaxometry and ^1H high-field NMR spectroscopy allows a separate analysis of the effects of the plasma treatments on the water and oil fractions. The two peaks corresponding to oil (lower T_2) and water (higher T_2) were clearly discernible in the T_2 distribution curves obtained for all analyzed samples (Figure 1); similar results were also achieved for the T_1 distribution curves. The water peak showed a reduction in its relative area, following the same trend discussed above for the water loss. As for the oil peak, all changes in the mean T_2 values were of minor significance considering the experimental uncertainties. The ^1H high-field NMR spectra also indicated that no significant chemical change on the oil fraction was produced by the plasma treatments. These results show that ^1H NMR measurements are indeed useful for the separate study of the effects of plasma and other treatments on crude heavy oils, without the need of laborious water separation procedures.

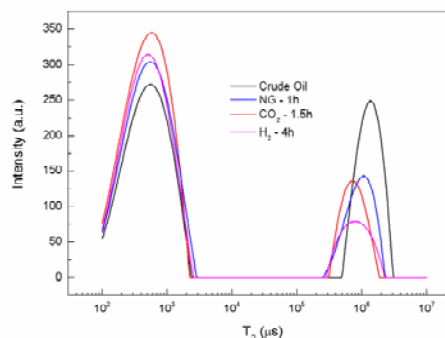


Fig. 1. T_2 distribution curves for the crude heavy oil and the plasma-treated samples.

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References

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