

Comparative study of new procedures developed to obtain the *n*-paraffin distribution of crude oils and its application to anticipate flow assurance problems

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Wax precipitation in crude oils by decreasing temperature is an important problem in the flow assurance field. Wax precipitation produces important economical losses, even leading to stop production. This is a well-known problem within the petroleum industry, and big research efforts are being made on developing procedures to anticipate potential wax deposition problems. The use of thermodynamic models [1] is the most common approach to carry out the prediction of the main variables involved in the wax deposition process: the wax appearance temperature (WAT) and the wax precipitation curve (WPC). However, because of the complex composition of crude oils, these models require a detailed, and very often hard to obtain, input. Typically, the *n*-paraffin distribution, the molecular weight and the total wax content of the crude oil is required.

The main limitation of this approach is to obtain an accurate determination of the *n*-paraffin distribution. Usually, experimental methods based on gas chromatography (GC) have been used. However, these methods are limited especially in the determination of heavy *n*-paraffins because of the low signal/noise ratio obtained. Very often, such determination is completed including empirical extrapolation procedures. Recently, a method based on Differential Scanning Calorimetry (DSC) has been successfully used to determine the *n*-paraffin distribution for petroleum fractions [2]. The main limitation of this experimental technique for crude oils is the low intensity and broad signal produced during the wax precipitation by decreasing temperature.

In order to solve such experimental limitations, in this work a concentration of the *n*-paraffins was carried out previous to the analysis and, for that reason, the isolation of the saturate fraction from the crude oil was attempted to obtain accurate *n*-paraffin distributions.

Two different methods (method A and B) were tested to separate the saturate fraction. Method A involves a previous removal of asphaltenes using *n*-pentane, whereas the saturate fraction is straightforward separated from the raw crude oil in method B. Wider *n*-paraffin distributions for the saturate fraction isolated by method B were obtained. DSC analysis of the saturate fractions showed a double peak at high temperature for that isolated by method B. This double peak was also detected for raw crude analysis, but not for saturated fraction obtained by method A, revealing a loss of heavy paraffins when using method A. This hypothesis was confirmed by gas chromatography-mass spectroscopy (GC-MS) analysis of the asphaltene fraction separated by method B, since the presence of C₂₄₊ *n*-paraffins was shown.

n-paraffin distribution for the crude oil was calculated using the saturate fraction separated by method A and B. The molecular weight of the crude oil was determined by gel permeation chromatography (GPC). A thermodynamic model was applied to estimate WAT and WPC of the crude oils. Obtained results were compared to experimental pour point (where is supposed to precipitate between 2 and 3% of solids), total wax content at -20°C and WPC.

References

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