P341-TH

CHARACTERIZATION OF ACIDIC COMPOUNDS IN BIODEGRADED OILS

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Nowadays, one of the greatest concerns of the oil industry is the acidity of crude oils, particularly in biodegraded or immature reservoirs. In most of the cases, this acidity is caused by what is called in the literature "naphthenic acids", which are, in reality, the carboxylic acids. Each step of the oil industry is concerned by the influence of this class of compounds: wettability alteration, destabilization of water/oil emulsions (Acevedo *et al*., 1999), corrosion of refinery units of heavy degraded oils (Laredo *et al.*, 2004). Therefore, acidic crude oils have a lower price due to these industrial risks. Predicting the quality of the oil in place before drilling, especially in deep offshore, is as important as predicting its volume. Consequently, the quality of the oil being directly linked to the acid molecules, particularly in biodegraded reservoirs, a qualitative and quantitative evaluation of the acidity has to be taken into account.

Total acidity (Total Acid Number) is routinely measured by a standardized method (ASTM D 974 or ASTM 664) based on a titration by KOH. It has been clearly demonstrated that a strong correlation exists between the TAN and the concentration of carboxylic acids in the crude oils and between the carboxylic acids content and the degree of biodegradation (Meredith *et al.*, 2000). However, in the range of 0.5 to 1.0, TAN of some oils does not correlate with the carboxylic acids amount showing that a more detailed approach is necessary. A molecular characterization but also a study of the mechanisms and kinetic parameters of the formation of such molecules are necessary.

A liquid-liquid extraction of the acidic compounds, followed by an esterification and a GC/MS analysis is widely used in the literature to characterize these compounds, but presents several drawbacks (unresolved signal with high biodegraded oils, lost of the heavier part of the sample in the column,...). New techniques as Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR MS) can overcome some of these inconvenient and provides very detailed information (Hughey *et al*., 2007) but the instrument is very expensive and it is challenging to find the right operating conditions.

The aim of the present work was to develop a new characterization schema, qualitative and quantitative, based on an extraction of the carboxylic acids followed by a derivatization and a reduction to hydrocarbons in order to perform a group type analysis by direct inlet mass spectrometry. The originality of such analytical procedure was to convert the total fraction of carboxylic acids into hydrocarbons without chemical side effect in order to use conventional techniques such liquid chromatography fractionation and quantitative mass spectrometry analysis for characterization. Group-type analysis gives an overall composition of the total fraction. As a matter of fact, the major advantage of direct inlet mass spectrometry is to be able to analyze compounds with a final boiling point near to 660°C (equivalent to C60) compared to GC, which is widely used as acid characterization, where only light compounds (up to C35) can be eluted from the column. The second advantage is the determination of hydrocarbons repartition by group type analysis. The saturates are analyzed in term of paraffins (n and iso) and cycloalcanes with one to 6 rings in % w/w (ASTM D2786-80, 1980) and the repartition of aromatics in 28 families (13 pure aromatic compounds (with 1 to 5 condensed rings) and 15 sulfured and disulfured aromatic compounds) is obtained (in %w/w) (Fafet *et al.*, 2000). Consequently, these two overall characterization can be further used for oil typing in terms of source or biodegradation alteration.

Each step of the protocol was validated with model compounds and quantitative accuracy was checked with a commercial mixture of naphthenic acids (Fluka).

This protocol was applied to several oils coming from the same basin but with different levels of biological alteration in order to implement the results in a basin model. Results show an increase of the total amount of carboxylic acids, a decrease of the acyclic species and an increase of the multi-ring compounds when the biodegradation level increases.

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