ESR Analysis of Asphaltene and Vanadium in Crude Oil Can Determine its Quality

Roughly one-third of the world's energy currently comes from crude oil. The quality of oil is determined by its chemical composition, which can affect its processing, performance, and market price. Therefore, qualitative and quantitative oil condition monitoring is essential.

The component that has the largest influence on oil quality is asphaltene, the heaviest fraction of crude oil. Asphaltene is made up of a complex mixture of compounds with polyaromatic rings and aliphatic side chains, combined with trace amounts of vanadium and nickel. Small concentrations of asphaltene can easily aggregate, leading to an increase in viscosity and resulting in plugging wellbores and flowlines during oil extraction and processing. In addition, asphaltenes can also deactivate catalytic reactions during upgrading and refining processes.

Analyzing the asphaltene concentration in the complex mixture of hydrocarbons in crude oil is difficult, especially for online monitoring. Traditionally, the physical properties of the oil, such as viscosity and dielectric constant, were measured and these data was used to determine the underlying chemical composition. And when specific asphaltene analysis has been performed, it is often in model systems or in samples that have been diluted into simple solvents.

Asphaltene and Vanadium have Characteristic ESR Spectra

The introduction of electron spin resonance (ESR) or electron paramagnetic resonance (EPR), has enabled asphaltene to be directly characterized. This technique provides high-resolution and quantitative data, which gives real dynamic information within the local environment. Furthermore, ESR is a non-destructive method and requires no sample preparation.

making it possible to determine the amount of adulterant present from the ESR signal intensity at 2 minutes (Figure 2).

Figure 1

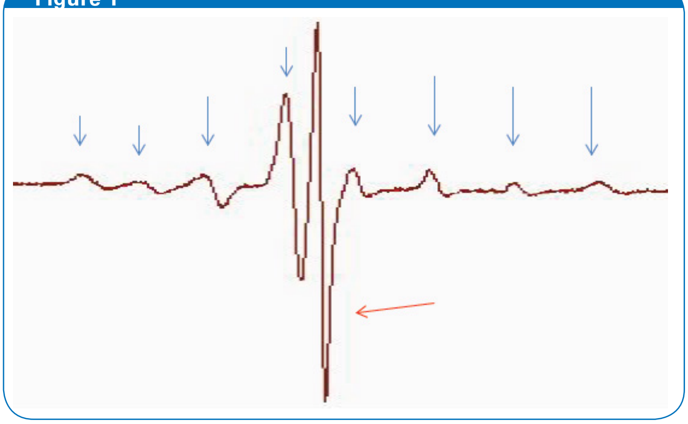

Figure 1. The characteristic ESR signals of the organic asphaltene free radical (red arrow) and the vanadyl porphyrin (blue arrows).

ESR uses the resonant absorption of microwaves within a static magnetic field to measure molecules with unpaired electrons and systems containing paramagnetic centers. Asphaltenes have organic free radicals in their polyaromatic core, which gives a characteristic ESR signal at g = 2.0032, making them readily identified in crude oil.

The amplitude of this peak corresponds to the concentration of asphaltene in the sample, so this technique can also be used for quantification. In addition, ESR can also detect vanadium, which is observed as a vanadyl porphyrin and appears as eight broadly spaced, narrow peaks in a similar region to the asphaltene organic free radical signal.

ESR can Analyze Specific Characteristics of Crude Oil

By monitoring various characteristics of these constituents, a greater understanding of the composition and chemical changes in crude oil can be achieved. Previously, ESR has been able to differentiate between different types of crude oil, but in recent years analysis of more specific criteria has been performed.

One of the main processes that changes the composition, and therefore the quality, of crude oil is biodegradation. In this process, hydrocarbons are oxidized to produce CO2 and organic acids, which leads to a decrease in the concentration of saturated and aromatic hydrocarbons and an increase in viscosity, metal content, and acidity.

Recent work compared this process in three Brazilian oils by monitoring the presence of organic free radicals and vanadyl species, associated or not with porphyrinic compounds using ESR. This method allowed the two biodegraded samples to be differentiated from the non-biodegraded sample through signal quantification values, as well as from each other.

Temperature is also known to affect the behavior and structural properties of organic free radical species in crude oil, impacting the quality. Research into these changes was recently performed using in situ ESR monitoring on different fractions of a crude oil sample with a temperature range of 293–673 K.

For all fractions, the increase in temperature resulted in the increase of organic free radial species, however, the mechanisms by which this process occurs were found to be different depending on the fraction. The atmospheric residue and crude oil fractions showed similar behavior, with the generation of organic free radicals around 433 K, while the generation of organic free radicals in the vacuum residue appeared to be a multistep process.

Bruker's MicroESR Enables Real-Time Analysis of Crude Oil Composition

The majority of ESR spectrometers are large, bulky instruments, limiting their ability to be used for online real-time analysis of crude oil. However, the advances in technology for optical and wireless communications have enabled Bruker to develop the smallest ESR spectrometer on the market – the microESR, a small, portable spectrometer with a 30.5 x 30.5 x 30.5 cm3 footprint and a mass of only 10 kg.

The microESR does not require any regular maintenance or special installation. The microESR also provides an easy software workflow for ESR data acquisition, processing and analysis.

With the recent advances in ESR use for crude oil analysis, the microESR can be used as a tool for online monitoring to characterize the chemical composition during exploration, production, and refining operations. This analysis can be used for many applications, including the assessment of the artificial aging of the oil, as well as anticipating problems that may occur further down the operation process.

References

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