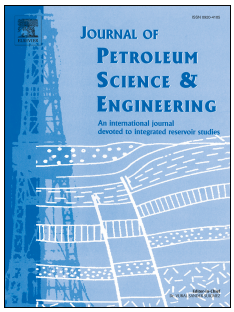
Accepted Manuscript



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PII: S0920-4105(16)30655-6

DOI: 10.1016/j.petrol.2017.06.007

Reference: PETROL 4019

To appear in: *Journal of Petroleum Science and Engineering*

Received Date: 11 October 2016

Revised Date: 16 January 2017

Accepted Date: 2 June 2017

Please cite this article as: Flórez, M., Guerrero, J., Mejía-Ospino, E., Cabanzo, R., SARA analysis and Conradson carbon residue prediction of Colombian crude oils using PLSR and Raman spectroscopy, *Journal of Petroleum Science and Engineering* (2017), doi: 10.1016/j.petrol.2017.06.007.

SARA ANALYSIS AND CONRADSON CARBON RESIDUE PREDICTION OF COLOMBIAN CRUDE OILS USING PLSR AND RAMAN SPECTROSCOPY

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Abstract: Raman spectroscopy generates a large volume of information at the molecular level of crude oils, which processed using chemometric methods allows building models to predict their physicochemical properties, facilitating to make decisions in refining processes for obtain high-value products efficiently and minimal environmental impact. In this work, the Raman spectra of crude oils from different regions of Colombia and Partial Least Square Regression (PLSR) were used to determine the fractions of saturates, aromatics, resins, asphaltenes (SARA analysis) and Conradson carbon residue (CCR), which were determined complying with the standards established by the American Society for Testing and Materials (ASTM). The dimensionality of the model was determined according to the root mean square error of cross validation (RMSECV), the coefficient of determination (R^2) and the correlation between consecutive pairs of regression vectors.

1. Introduction

The knowledge at the molecular level of crude oils and its relationship with the physicochemical properties is essential because it allows generating innovative proposals in production, transports and refining processes, obtaining efficiently high-value products. SARA analysis is a typical characterization process of crude oils, that distinguishes the samples according the chemical affinity with solvents of varied polarity and surface active solids (chromatographic methodology) in terms of saturates, aromatics, resins and asphaltenes present in crude oils (Speight, 2003)(De Oliveira, Vazquez, Verstraete, & Kolb, 2013). The saturate fraction is the least polar fraction of the crude oils. This fraction is mainly constituted by paraffinic and naphthenic molecules with small amounts of heteroatoms. Aromatics and resins are both intermediate fractions; however, the first fraction is the lightest and less polar than the second one. In fact, aromatics are composed of molecules with a moderate concentration of heteroatoms (essentially sulfur), while the molecules with a higher concentration of heteroatoms (sulfur and nitrogen) can be found in the resin fraction. The asphaltenes is the heaviest and most polar fraction of crude oils, and they contain high concentrations of sulfur, nitrogen, oxygen and metals organized in a large variety of chemical functions (Sheu, 2002).

SARA analysis methodology is standardized by the American Society Test and Materials (ASTM D4124-09, ASTM D2007-03) (ASTM D4124, 2009; Pressure, 2007). These procedures generate high costs, because require large amount of samples and solvents. Moreover, the whole process takes on average two days per sample and during the analysis a large amount of environmental hazard solvents are used, creating disposal problems. Other technical hitches of these processes are related to the lack of automation, poor repeatability and reproducibility of results.

Several spectroscopic techniques, NIR-Near Infrared, Fourier Transform Infrared (FTIR), Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR), Raman, Nuclear Magnetic Resonance, Gas and Liquid Chromatography and Mass Spectrometry (MS), are being used for the characterization and classification of crude oils and the analysis of products of the refining process (Wilt, Welch, & Rankin,