

Structural Characterization of Asphaltenes Obtained from Hydroprocessed Crude Oils by SEM and TEM

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Asphaltenes from Maya crude and its hydroprocessed oils at different reaction conditions were precipitated and studied by scanning and transmission electron microscopy (SEM and TEM). In order to better understand the changes occurred in asphaltene structure during hydroprocessing the crude oil fractionation procedure with solvents was used to separate asphaltenes based on their solubility properties. Different asphaltene morphologies were observed depending on the mixture of solvents used for fractionating asphaltenes and reaction conditions at which crude oil was hydroprocessed. A comparison between asphaltenes from hydroprocessed and pure Maya crude oil was carried out on the way to distinguish morphological changes at microscopic level. It was observed that removal of alkyl chains during hydroprocessing makes asphaltenes suffer a rearrangement in solid state favoring stacking of aromatic cores as determined by TEM. SEM microscopy allowed different fractions of asphaltenes for seeing that they are constituted by agglomerate particles, porous structures, and smooth surfaces.

1. Introduction

Asphaltenes are complex molecules which are precipitated from oil, e.g., petroleum and its residual, by adding a paraffinic solvent such as *n*-heptane. The most widely known and accepted definition of asphaltenes is based on their solubility properties, so that asphaltenes are soluble in aromatic solvents such as toluene and insoluble in paraffins such as *n*-heptane. In a complex crude oil mixture where thousands of compounds may suffer aggregation, thus, it is mandatory to explore different and more sensitive techniques to discriminate between various molecules in the solid fraction.¹

To obtain better knowledge of structural parameters of highly carbonaceous materials such as asphaltenes, different analytical techniques have been used, e.g. X-ray diffraction (XRD), Raman spectroscopy (RS), high-resolution transmission electron microscopy (HRTEM), among others. XRD is useful for determining interlayer spacing, crystallite size, and crystallite diameter. Some attempts have been carried out in order to compare structural parameters obtained from XRD and HRTEM but only in a qualitative way.² The diameter of the layer determined by HRTEM is larger than that obtained by XRD, and hence, a direct comparison is not appropriate. However, for comparison purposes only those fringes in the linear portion obtained at high resolution by HRTEM must be considered to obtain a qualitative analysis of the morphology at the atomic level. For obtaining images from HRTEM it is necessary that the sample

be thin and partly transmits the electron beam because overlapping would occur if the sample is not an ordered structure.³

Sharma et al.⁴ analyzed model compounds by HRTEM with similar structures to asphaltenes and concluded that the presence of alkyl chains disrupts the stacking. On the contrary, structures having only aromatic cores are able to stack easily. This can be extended to asphaltenes which are prone to stack if alkyl chains are missing. Other authors¹ studied the morphology of asphaltenes by HRTEM and SEM (scanning electron microscopy). In their study, asphaltenes were carefully separated from resins to obtain pure asphaltenes and elemental analysis was performed on them. It was found that when resins are completely separated from asphaltenes the purified asphaltenes consist of carbon structures carrying S, V, and Si, related to fullerenic carbon. Most of the sample was amorphous without any defined structure as observed by SEM. Analysis by HRTEM showed graphene-like layers having a morphology similar to a cauliflower with a separation between layers of 0.39 nm. Mordkovich et al.⁵ also reported the existence of a two-shell fullerene with a size of 1.4 nm.

Confocal laser scanning microscopy along with fluorescence microscopy is another tool that allows for directly observing asphaltenes into their natural media. Fluorescence properties of asphaltenes can be used to examine their dispersion and structure in bitumen directly as reported by Bearsley et al.,⁶ who stated that the size of fluorescing particles ranges from 2 to 7 μm .

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