

What's in your asphaltenes? Automated solubility based separations provide more information than gravimetric techniques.

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Precipitation and filtration of asphaltenes is performed by a variety of standard methods, and different methods can provide different results. The term "asphaltenes" is a catch-all designation for insoluble material. Although most pericondensed aromatic components precipitate with the asphaltenes, many can remain in the maltenes due to solvation and association effects. Asphaltenes also may contain significant wax content, depending on the oil. The associated complexes in heptane asphaltenes can also contain some entrained heptane soluble components. Nevertheless, these are all asphaltenes using the definition of asphaltenes as heptane insoluble / toluene soluble material. SARA (saturates, aromatics, resins, and asphaltenes) methods involve gravimetric precipitation of asphaltenes followed by separation of maltenes into three or more subfractions; however, there is no provision in these methods for separating asphaltenes further into chemically meaningful subfractions. As insoluble material comprised of a variety of associated chemical species, it is generally understood that concept of asphaltenes has little chemical significance.

A new solubility-based on-column precipitation and re-dissolution technique developed at Western Research Institute allows for the rapid separation of the polar, pericondensed, and wax materials in oils into chemically meaningful subfractions [1]. A stainless steel column packed with 40-60 mesh polytetrafluoroethylene (PTFE) is used to conduct the automated separations using mg quantities of sample. The column packing acts as an inert three-dimensional filter medium. Although high performance liquid chromatography (HPLC) equipment is used, the new technique does not involve chromatography; it is strictly solubility based on a molecular level. Detection is by evaporative light scattering (ELSD) and optical absorbance.

One of the automated methods is called the Asphaltene Determinator. This separation is used to rapidly determine asphaltene content, and to measure subfractions comprising asphaltenes and resins / polars material. Either whole oil samples or precipitated asphaltenes can be separated. The on-column precipitation is conducted with heptane at 30 °C. Once the heptane soluble material elutes, the heptane insoluble components are re-dissolved in

sequence using step changes of solvents of increasing solubility parameter to provide fractions comprising cyclohexane soluble, toluene soluble, and methylene chloride:methanol (98:2 v:v) soluble components of the sample. The fractions represent different degrees of polarity and pericondensed aromatic structure for components in the solubility / polarity continuum that comprises the oils.

Results can be used to track pyrolysis severity to improve the efficiency of atmospheric and vacuum distillation processes, and also to evaluate the thermal history of any petroleum oil [1]. The data can be used to correlate with gravimetric asphaltenes content [2]. However, gravimetric asphaltenes contain entrained associated materials that can be separated further with the Asphaltene Determinator method, so such correlations with bulk gravimetric separations are approximate at best. Emulsion stabilizing components of oils can be studied with the method. Differences in amounts and internal molecular distribution of asphaltenes and SARA resins materials have been observed in supernatant oils and the corresponding oils from oil/water emulsion rag layers.

Another automated method is called the Waxphaltene Determinator. This is used to measure both n-paraffin and branched waxes and asphaltene component molecules with a single injection [3]. The separation is performed with an initial precipitation in methyl ethyl ketone (MEK) at -24 °C. Waxes and asphaltenes precipitate, and the MEK maltenes elute. The precipitated material is then re-dissolved and eluted with heptane at -24 °C (branched waxes and polar components), heptane at +60 °C (n-paraffins), toluene at +30 °C (pericondensed asphaltene components), and methylene chloride:methanol (98:2 v:v) at +30 °C (pre-coke mesophase).

References

- [1] Schabron, J.F., Rovani, J.F. (2008) Fuel 87, 165-176.
- [2] Rogel, E., Ovalles, C., Moir, M., Schabron, J.F. (2009) Energy & Fuels 23, 4515-4521.
- [3] Goual, L., Schabron, J.F., Turner, T.F., Towler, B. (2008) Energy & Fuels 22, 4019-4028.