

## A fuller characterisation for a better understanding of instability risks of heavy petroleum products

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Instability of heavy petroleum products and fouling of process units are major industrial concerns. Because of the lack of understanding of their driving mechanisms, better characterisation and deeper understanding of these risks are required.

At IFP, the classical characterisation techniques for managing these plugging risks are based on spot tests and on measurements of total sediments (IP375). Although, with experience, they can be good means of following sediment accumulation in units or critical evolution of products, they are often not reliable enough as heavy products encompass a wide molecular composition.

**New analytical techniques have been investigated to get a more complete picture of the critical factors that explain instability behaviours.**

To replace manual spot tests, S-value (ASTM D7157) has been chosen to give a more detailed characterisation of heavy fractions. Similar to the manual Martin-Bailey analysis, the technique gives semi-automatically information about asphaltene's peptisability, oil's peptising power and the general stability of product (Sa, So & S). In comparison, the data is now both more practical and more reliable. It is proving to be a useful tool for process units follow up.

To replace sediment measurements, an optical microscope methodology has been developed to improve the quality and the quantity of information available. It also quickens the results and reduces the sample volume required. The technique does not exactly give the same information: instead of a weight percentage of sediments, the microscope only indicates a 2D surface percentage of sediments in the pictures, but with better fidelity. This technique can also give size distributions, mean distances between aggregates, aggregates' density...

These characterisations are necessary to gain fuller understanding of the nature of the products. The real need of process engineers though is to be able to anticipate any critical situation while maximising the heavy fuel conversion. In order to predict the stability limit of a product, a mechanistic interpretation of its aggregation is necessary, as well as the corresponding characterisation.

The aggregation of asphaltenes in maltene can be described through the determination of the van der Waals forces involved between molecules, based on the following equation [1]:

$$C_{VDW} = 3k_B T a_1^6 \left( \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \right)^2 + \frac{\sqrt{3}}{4} h \nu_e a_1^6 \frac{(n_1^2 - n_2^2)^2}{(n_1^2 + 2n_2^2)^{3/2}} \quad (1)$$

$C_{VDW}$  : van der Waals interaction coefficient

$a_1$  : equivalent radius

$T$  : Temperature

$\nu_e$  : UV absorption frequency

$\epsilon$  : dielectric constant

$h$  : Planck constant

$k_B$  : Boltzmann constant

$n$  : refractive index

A classic assumption made is to consider only London's dispersion forces. But it is wrong to underestimate Keesom and Debye's polar forces [1]. Refractive index alone will not give a good understanding of the solubilising capacity of a solution (be it solvent or maltene). For instance, if THF, which has a poor refractive index compared to toluene or  $\alpha$ -methylnaphthalene, is a good asphaltene solvent, it is most certainly because of its higher polarity. Whereas  $CDCl_3$  can be considered a better solvent as it is the best compromise between the two forces (as illustrated in the table below) [3].

RMN-DOSY solvent	Toluene	THF	$CDCl_3$
solvent refractive index	1.4961 at 20°C	1.4076 at 21°C	1.4459 at 20°C
solvent dielectric constant	2.379 at 25°C	7.52 at 22°C	4.807 at 20°C
diluted/semi diluted asphaltenes state threshold	0.5%	2%	3%
aggregation threshold	0.75 - 3%	3 - 5%	5 - 10%

To complete the picture, it is therefore necessary to characterise both polarisability and polarity of maltenes and asphaltenes. To do so we are working on ways of measuring both asphaltenes' and maltenes' refractive index and dielectric constants. Dielectric constants are measured using complex impedance spectroscopy. Characterisation protocols and data results will be presented.

Combining these different techniques allows a better assessment of the multiple causes for instability and provides necessary data for predicting the evolution of products near their instability threshold.

### References

- [1] J. Israelachvili (1991) Intermolecular and surface Forces. London: Academic Press
- [2] L. Goual and A. Firoozabadi, (2002) AIChE Journal, Vol. 48, No.11.
- [3] E. Durand (2009) IFP Ph.D.