Determination of asphaltene aggregation kinetic by focused beam reflectance measurements

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This work deals with the determination of asphaltene aggregation kinetics using a focused beam laser reflectance (FBRM) instrument. Asphaltenes have been defined as the fraction of crude oil that is insoluble in normal alkanes such as n-heptane and soluble in toluene [1]. A closed stirred reactor has been used in order to determine the point of asphaltene precipitation onset of different crude oils. The procedure consisted on discontinuous additions (one each 20 minutes) of n-heptane in volume values of 0.1 mL per g of crude oil [2]. Once asphaltene onset has been determined, the aggregation kinetic of solids formed has been studied at different temperatures and ratios between volume of n-heptane and mass of crude oil (R, mL of n-heptane / g of crude oil). The time to reach the asphaltene aggregation equilibrium is higher as R is closer to onset.

The experimental data provided by the instrument is the chord length distribution as a curve. Aggregation kinetics has been followed through the time evolution of the zero-moment, M_0, which represents the integrated area of the curve normalized to the mass of crude oil.

The equation used to describe asphaltene kinetics has been the following:

$$M_0 = \frac{M_{0,\max} t}{t_{1/2} + t} \qquad (1)$$

Where $M_{0,max}$ is the asymptotic maximum value of zero-moment and $t_{1/2}$ is the time in which the half of this maximum value have been achieved.

Figure 1 shows an example of the fitting of this equation to actual data of asphaltene precipitation, including the values of the kinetic parameters. Figure 2 shows the dependence of $M_{0,max}$ on the n-heptane / crude oil ratio. The results indicate that the amount of precipitated solids increases for higher amount of alkane, but a hyperbolic trend to a maximum value is observed. The equation that describes hyperbolic trend has been the following:

$$M_{0,\max} = \frac{M_{0,m}(R - R_0)}{R_{1/2} + (R - R_0)} \qquad (2)$$

Where M_{0m} is the asymptotic maximum value of zero-moment and $R_{1/2}$ is the alkane / crude oil ratio to reach half of M_{0m} value. R_0 is the parameter that allows determining the model-predicted asphaltene onset.

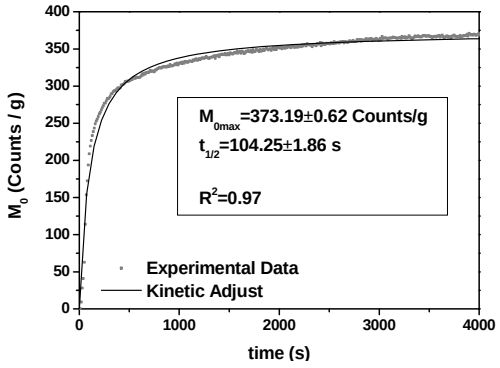

Fig. 1. Asphaltene kinetics for crude oil D-03/03, R=2 mL n-heptane / g crude oil (R_{onset}=0.9 mL n-heptane / g crude oil), 60ºC.

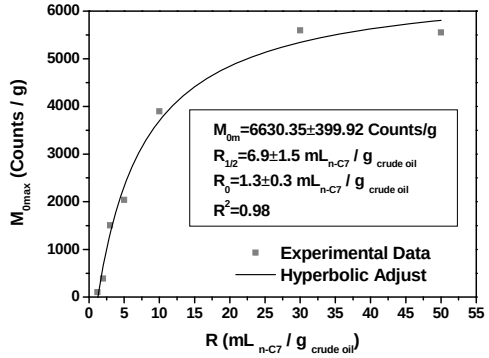

Fig. 2. Dependence of the kinetic parameter $M_{0,max}$ on the n-alkane/oil ratio at 60ºC.

Dependence of the inverse of the half time versus the n-alkane to oil ratio allows the estimation of the asphaltene threshold value by extrapolation.

References

[1] Mitchell, D. L., Speight, J. G. (1973) Fuel. 52, 149-152.
[2] Calles, J. A., Dufour, J., Marugán, J., Peña, J. L., Giménez-Aguirre, R., Merino-García, D. (2008) Energy and Fuels. 22, 763-769.