Fast Analytical Method for Asphaltene Polydispersity Description

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Abstract
Asphaltenes can be responsible for production shortfalls and various flow assurance related issues. However, in spite of years of studies, these issues are not yet correctly predicted as there is an interplay between thermodynamic and kinectic. An important part of the difficulty is that the asphaltene fraction is not well defined in terms of properties, outside of its percentage and solubility in n-alcanes. Various attends and methodologies have been developped to better quality the solubility and polydispersity of asphaltenes. One of the difficulty is that some of these methodologies can lead to being "overflown" with data.In this work, an HPLC-CAD analysis coupled with in-line precipitation and redissolution of asphaltenes allow for a fast and quantitative mapping of the polydispersity of an asphaltene sample through the definition of asphaltene classes based on their solutility profile. This methodology can be used for several applications, such as the evolution of samples coming from a field, the production chemistry studies during field developments, or R&D topics to better understand deposition and fractionnation.

Keywords
Asphaltene; Polydispersity; High-Performance Liquid Chromatography

Introduction
Asphaltenes are an important fraction of crude oils concerning flow assurance and production chemistry studies. Depending on their properties, and the solvency of the crude oil that contain them, they can be responsible for enhanced emulsion stability, or phase separate to precipitate or to form deposits.

Because their definition is mainly based on their solubility class ("Not soluble in heptane and soluble in toluene"), they are very often quite ill defined.

If procedures are well established in the community to compare their percentages between different systems (see for example [1]), this value alone is quite insufficient to describe both the risk of emulsion or of precipitation, as in particular it does not give any information on the "quality" nor the polydispersity of asphaltenes.

Very powerful analytical techniques such as FT-ICR MS spectroscopy have been developed and allow to have a very precise molecular description of the asphaltenes molecules [2]-[4]. But they can finally end-up with being "overflown" with information that make comparison between different asphaltenes very qualitative, one of the reasons being that they are not quantitative.

Others have tried to define asphaltenes and their solubilities through liquid chromatography and different detection methodologies [5]-[7]. These methods produce distributions of the composition of the asphaltenes, and they are at least semi quantitative. Other advantages of these methods are that they only require minimal crude oil samples and are quite fast.

Within TotalEnergies, a methodology was developed to grade the solubility of an asphaltene, whether it is contained in a crude oil or found in a deposit, through the measurement of its Asphaltene Solubility Class Index (ASCI).

As illustrated in [8], this method can be coupled to gravimetric precipitation methodology to describe the polydispersity of asphaltenes: it then gives very valuable information that allow for a fast comparison between various asphaltenes but is quite time consuming.

It was thus decided to try to develop an analytical methodology that would allow to quantitatively describe the asphaltene polydispersity for fast comparison between samples, while using minimal crude oil quantities and minimal times.

Methodology
The methodology is based on an in-line precipitation of the asphaltenes followed by re-solubilization using a mixture of one or more good solvents using aHigh-Performance Liquid Chromatography (HPLC) and a Charged Aerosol Detector (CAD).

The re-solubilization can be done in one single step or in multiple steps. This last allows us to build a solubility profile of the solids.

A precipitation cell has been specifically designed to ensure not only an efficient precipitation of the asphaltenes but also a proper mixing between heptane and toluene during the reelution of the precipitated asphaltenes [9]. More importantly, the area/volume ratio of the cell was optimized to avoid asphaltene adsorption and or adhesion on the surface of the cell. This leads to more accurate and reproducible analysis. A filter is positioned just after the precipitation cell to block the solids in a specific place of the system, allowing the proper re-solubilization and elution of the asphaltenes.

At the end of the analysis, Isopropanol is used to clean the filter, and a blank sample is run to ensure that there is no residual deposit prior to the next analysis.

The complete multiple step analytical protocol takes about 1h30 to 2 hours and is illustrated in Fig. 1. The one step analysis takes 20 to 30 min.
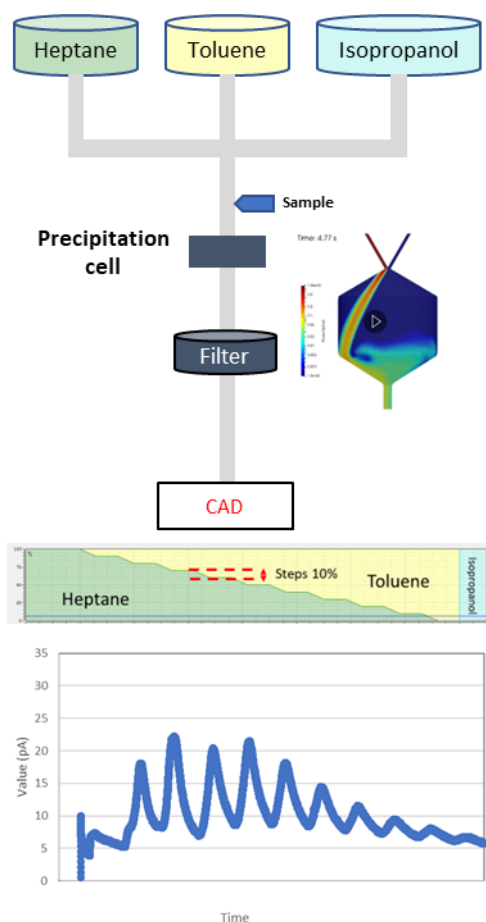

Figure 1. Schematic of the experimental procedure

First experiments show a non-uniform response of the CAD when analyzing asphaltenes from different crude oils. This non-universality might have multiple raisons: (a) presence of impurities inside the asphaltene fraction (maltenes), (b) the large definition of an asphaltene – probably different chemistries for a same solubility class, …

For a precise determination of the asphaltene percentage between different crude oils, one possibility is to compare the samples at various concentrations to a reference.

For the multiple step methodology, each step of increase in the toluene percentage corresponds to a 10% increase (or 2 ASCI notes) and can be integrated to give a quantitative description of the polydispersity of the asphaltenes from the sample as illustrated in Fig. 2.
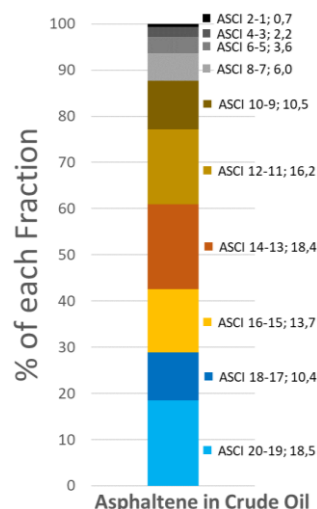

Figure 2. Example of the polydispersity of an asphaltene inside a crude oil – for each class, the number is the weight %

Results and Discussion

The analytical methodology has been applied to different cases from "applied" studies to more fundamental understanding.

A well in a field in western Europe was experiencing production issues. As it was known that the asphaltenes of that field were quite unstable, it was decided to follow their properties over time to make sure the operational issues were not due to variations in the asphaltene fraction.

Samples were taken over time and the analysis were performed following the procedure described earlier. Fig 3 gives the polydispersity of the samples taken over time by integrating the area of each peak, with the average given as the last bar: except for the last sample, there is little variation both in the amount of asphaltenes and their polydispersity.
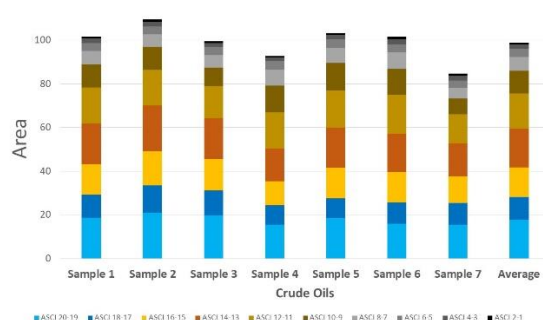

Figure 3. Quantitative repartition of asphaltenes from samples taken from the same well over time

When performing production chemistry studies, it can be interesting to find analogues between different crude oils. The methodology was used to

determine the polydispersity of asphaltenes from different crude oils in our portfolio. As it is illustrated in the figure below with graphs either for the area of each class or for the percentage, it is very fast to see that Crude 1 has a lot more asphaltenes than Crude 2, or that the asphaltenes from Crude 3 and Crude 4 are very similar in polydispersity.
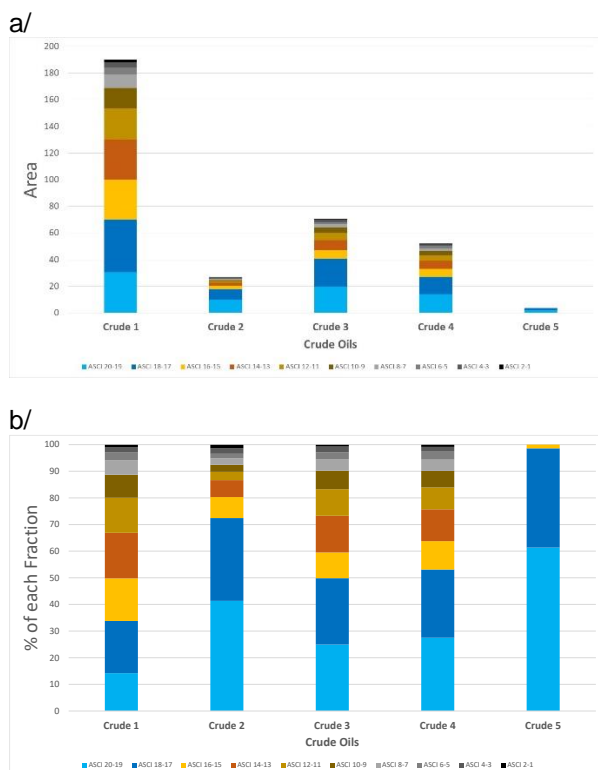
a/

b/

Figure 4. a/ Quantitative repartition of asphaltenes from different crude oils, b/ % of each asphaltene fractions in the asphaltenes

If Crude 1 is taken as a reference, it is possible to calculate the weight percent of asphaltene from the differences in the area of the peaks, as illustrated in Tab. 1. The agreement with the measured weight percentage by precipitation at a ratio of 1 to 20 with heptane is very good, except for Crude 3. A possible explanation for it would be a high level of coprecipitate species being entrained with asphaltenes.

Table 1. data on the asphaltenes in the different crude oils

	ASCI	%w Asph measured	Area CAD	%w Asph calc
Crude 1	9	12	190	12
Crude 2	18	2	27	1.7
Crude 3	12	10	70	4.5
Crude 4	12	4	52	3.3
Crude 5	20	0.1	4	0.2

The last example of the use of the methodology was to perform a test complementary to the polydispersity studies performed in [8]. Crude A in [8] is Crude 1 in this paper. In [8], we analyzed the asphaltenes precipitated with different heptols,

leading to a fractionation of the whole asphaltenes. As illustrated in Fig. 5 :
- if an heptol at 40% of Heptane (or ASCI 8) is used, no asphaltenes precipitate.
- if an heptol at 45% of Heptane (or ASCI 9) is used, a first fraction of asphalene precipitate that is so "bad" that they are even not soluble in Toluene, and their ASCI is 0.
- if an heptol at 65% of Heptane (or ASCI 13) is used, 5% of Asphaltenes precipitate and, once resolubilized in Toluene, their ASCI is 7 (lower than the whole asphaltenes.
- Finally, in pure Heptane (or ASCI 20), the whole asphaltene precipitate with the properties indicated in Tab. 1.
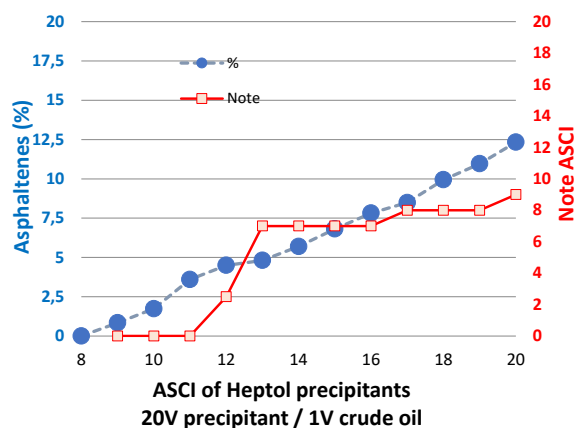

Figure 5. Quantities (w%) and ASCI of the asphaltenes precipitated from Crude A in [8] for different heptols

Here, we used the developed analytical protocol to perform the complementary tests: instead of analyzing the precipitates, we analyzed what remained in solution in the Heptols.
Before ASCI 10 for the Heptol, all the asphaltenes remain in solution (there is no precipitation) and the amount (area) as well as the polydispersity remain constant, and very similar to what is illustrated in Fig.3 for the same crude oil.
After ASCI 10 and increasing with the ASCI of the precipitant, more and more asphaltenes precipitate, reducing the amount remaining in solution (lower area) and as the "least soluble" asphaltenes precipitate first, the "quality" of the asphaltenes remaining in solution improves as shown in Fig 6. b/. Interestingly, Asphaltene molecules with ASCI below 12-10 are completely eliminated from the small fraction remaining soluble in heptane, but they are still about 30% of this small fraction composed by asphaltene molecules having an ASCI between 14 and 10.
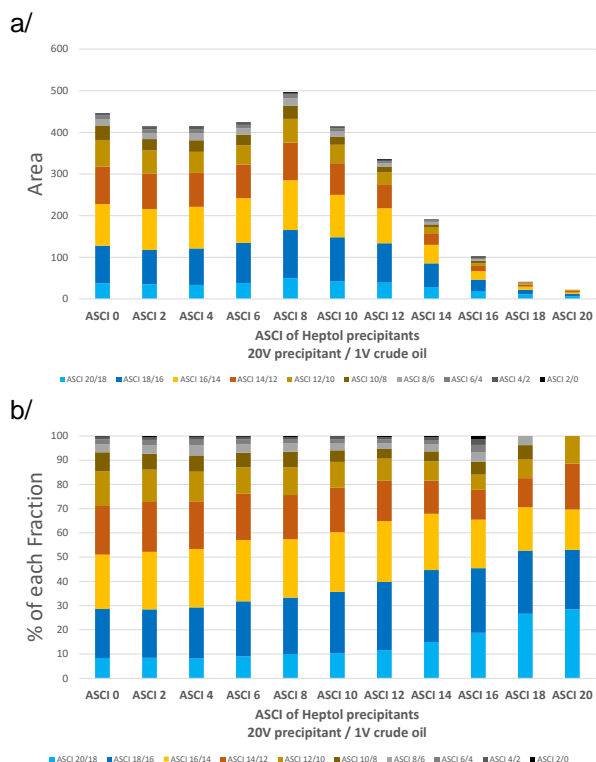
a/

b/

Figure 6. a/ Quantities (area) and polydispersity of the asphaltenes from Crude 1 remaining in solution in the various Heptols, b/ Polydispertity in %

Conclusions

The development of an analytical methodology based on HPLC-CAD and in-line precipitation/resolubilization of asphaltene fractions allows to determine quickly and quantitatively the polydispersity of asphaltene samples.

The methodology can be applied in different cases, from follow-up of field samples to production chemistry studies or R&D studies.

A better knowledge of the properties of the asphaltene fraction, not seen as a single component, will be key to better predicting and anticipating potential flow assurance issues associated with asphaltene precipitation or deposition.

Acknowledgments

Responsibility Notice

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