

Procedure for Measuring the Onset of Asphaltene Flocculation

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Introduction

Asphaltene stability is a function of composition, temperature and pressure. In the procedure outlined here, dead crude oil is titrated at ambient conditions with normal alkanes to find the first appearance of asphaltene aggregates. Microscopic aggregates are detected optically with transmitted light, setting an effective lower limit of about 0.5 μm on the size that can be reliably discerned. For some oils, the first appearance of aggregates is readily distinguished from clear solutions with only slightly less alkane precipitant. In other cases fine particles appear before aggregates are observed and it is more difficult to define an onset condition. In the latter case, two onset conditions can be defined: (1) the conditions where fine asphaltic particles first appear or *onset of fines*, and (2) the conditions where those particles first begin to aggregate or *onset of aggregates*. Between these conditions is a more or less continuous increase in the amount of particulate material.

The solubility conditions in the dead oil sample and at the onset are quantified by refractive index (RI) measured at 20°C at the wavelength of the sodium-D line (589 nm). Quantities of interest include RI of the dead oil sample (RI_{oil}) and RI of the mixture of oil and alkane at the onset of precipitation (P_{RI}). In effect, RI is a surrogate for the solubility parameter (δ), used because it can be readily measured whereas δ must be estimated for complex fluids like crude oils. For nonpolar liquids including crude oils, δ can be calculated from RI using an empirical correlation.

Interference is often encountered from asphaltene aggregates and other particulates and emulsified matter that are present in the dead oil samples, as received. Methods for dealing with samples that contain emulsions and/or particulates are included in this procedure.

Asphaltene flocculation can be a slow process, especially near the onset point. In most titration techniques the precipitant is added fairly quickly, which probably leads to an overestimate of the amount of precipitant at the onset point and a corresponding overestimate of asphaltene stability. Experience has shown that one day of aging is the minimum amount of time needed to make a reliable judgment about the onset; longer times would be better, but are seldom practical.

The overall asphaltene onset characterization scheme is outlined in Fig. 1 and discussed in detail in the sections that follow.

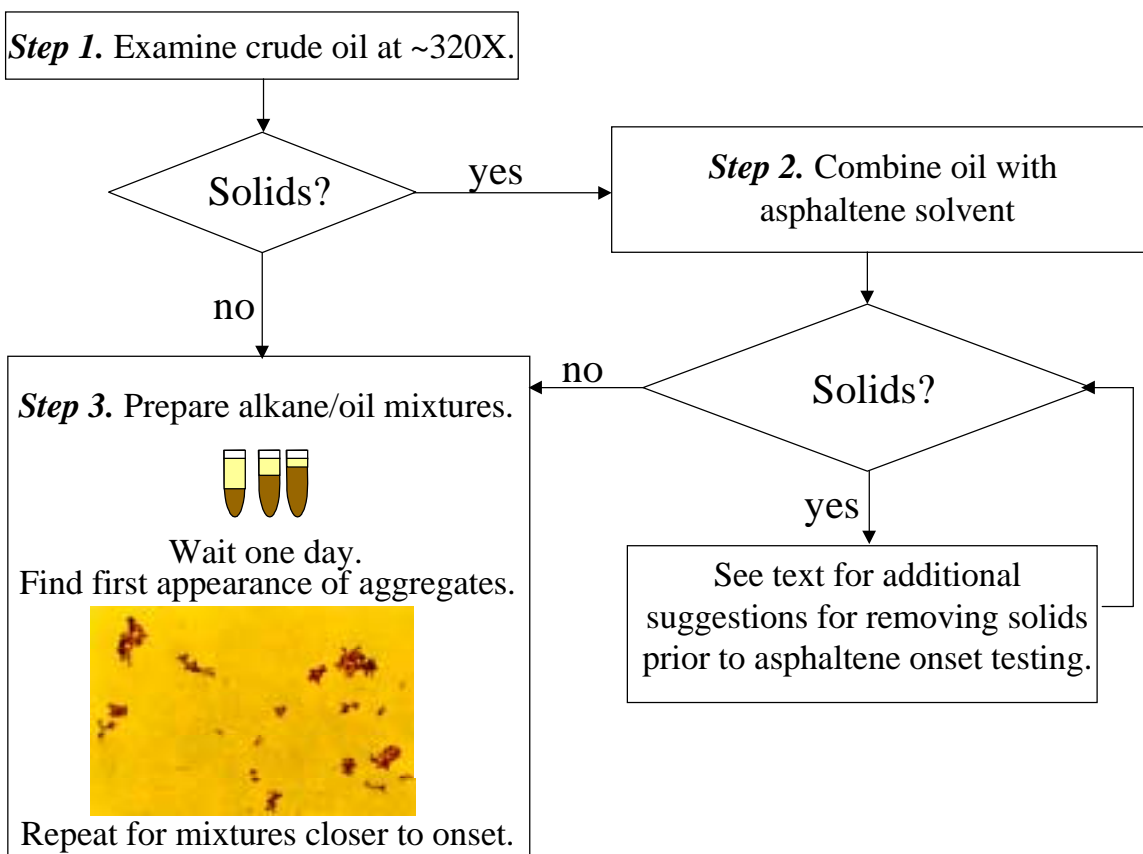


Figure 1. Outline of the asphaltene onset determination scheme.

Step 1. Microscopic examination

A drop of dead crude oil is placed on a microscope slide, covered with a cover slip, and observed microscopically at a magnification of about 320X. If the sample is clear and free from any particles, no special pretreatment is required. Skip Step 2 and proceed to Step 3.

Often crude oils contain aggregated asphaltenes, wax crystals, emulsified water, and other unidentified solid particles. The aggregated asphaltenes may appear as large aggregates, small aggregates, or individual fines or particles. Asphaltenes can often be observed adhering to one another. They can be distinguished from wax crystals by observing between polarizing filters oriented at 90° to one another. The crystalline waxes can pass polarized light and appear as bright spots whereas asphaltenes are amorphous and cannot be seen. Highly spherical objects are likely to be emulsified liquids. These oils cannot be used directly to find the onset point induced by adding n-alkanes since the existing aggregates or particles may obscure the onset observation. Strategies for removing sources of interference are outlined in Step 2.

Step 2. Redispersing of asphaltene aggregates

Asphaltene aggregates, waxes, and other particulates, could be removed mechanically by filtration or centrifugation. A better strategy, however, is to redisperse the asphaltene aggregates by addition of a good asphaltene solvent. This option is preferable because all the oil components are retained. Aromatic compounds, such as toluene or 1-methylnaphthalene (1-MN), are good asphaltene solvents. 1-MN is the stronger solvent, but it is also more viscous than toluene so the time required to disperse the asphaltenes is longer. The value of P_{RI} is shifted more by addition of toluene than by 1-MN. The value of P_{RI} obtained from a 50:50 mixture of oil mixed with 1-MN is normally only slightly different from the value of P_{RI} that would be measured for the crude oil without added solvent. If time and oil sample volume permit, however, a more accurate value of P_{RI} can be obtained by testing two or more mixtures with different ratios of oil to 1-MN. P_{RI} can then be evaluated as a function of the amount of added solvent and extrapolated to the value of P_{RI} for oil with no added solvent.

For oil samples with asphaltene aggregates and/or other particulates or emulsions, the following steps are recommended:

- 2.1 Prepare a 1:1 mixture of oil with 1-MN. Stir the mixture for one to two days, checking for particles at $\sim 320\times$. If no asphaltenes are visible proceed to Step 2.5.
- 2.2 If complete dispersion is not achieved, agitate the mixture in an ultrasonic water bath for several hours. If asphaltenes disappear, proceed to Step 2.5.
- 2.3 If asphaltene are still not completely dissolved, heat the mixtures to 60 to 70°C for several hours in sealed vials, taking care to prevent evaporation. If asphaltenes disappear, proceed to Step 2.5.
- 2.4 If none of these treatments redisperses the asphaltenes, add a known amount of 1-MN to the mixture to further reduce oil:1-MN volume ratio and repeat the sequence starting at 2.1 above.
- 2.5 If waxes remain after asphaltenes are completely redispersed, heat the solution as described at 2.3 above. Usually this will be sufficient to dissolve the waxes, which may reappear, but slowly so that they do not interfere with the onset tests. If there are no emulsions, proceed to Step 3.
- 2.6 Emulsified water may segregate from the oil and collect as a sediment on the bottom of the container during steps 2.1 to 2.5. If the sediment is gray or white in color, most asphaltenes that once may have collected at the oil/water interface have been redispersed. Proceed to Step 2.7. If the sediment is brown, some of the asphaltene fraction may remain associated with the emulsion interfaces. Add a large volume of distilled water to the oil/1-MN mixture. Agitate in an ultrasonic water bath for about 30

minutes. This washing step should help to break the original emulsion, releasing the asphaltenes. The mixture can then be separated as described in Step 2.7.

- 2.7 If no emulsified droplets remain suspended, carefully separate the supernatant and proceed with Step 3. If emulsified droplets remain in suspension, centrifuge at 2000-3000 rpm for several hours in sealed centrifuge tubes. Separate the supernatant and proceed with Step 3. This step should also remove extraneous inorganic solids and extremely refractory organics (known as carbenes and carboids).

Step 3. Measure onset of asphaltene flocculation

The onset condition (or conditions—if both the *onset of fines* and *onset of aggregates* exist) can be determined to a reasonable tolerance by examination of mixtures of oil and precipitant that vary by 1% (by volume) in composition. If aggregates are observed in a mixture consisting of 50% oil (or oil/1-MN mixture) and 50% heptane, but a mixture with 51% oil and 49% heptane is clear, then the 50:50 mixture would be considered to be the onset mixture.

The onset search can be refined in a series of steps. If oil is the limiting factor, fewer mixtures would be included in each step and the number of steps would be increased. The extreme example would be a search by the bisection method beginning with a 50:50 mixture of oil and precipitant, followed by either a 25:75 or 75:25 mixture depending on whether asphaltenes were observed in the first mixture. If there is plenty of oil, time can be saved by making more mixtures in each step. In the extreme case, 99 separate mixtures would be prepared in the first step if the 1% tolerance level were the target. Clearly this is impractical and the most efficient search strategy lies between the two extremes.

As a compromise between conserving oil and minimizing time, begin with a coarse screening, consisting of a series of seven widely spaced mixtures (oil:precipitant = 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20). Note that “oil” refers either to the original oil or the mixture of oil and solvent prepared in Step 2. Subsequent mixtures would be selected on the basis of the results of the coarse screening step. For precipitation with n-heptane, the onset is often found between 20:80 and 40:60, so oil might be conserved by beginning with mixtures in that range.

- 3.1 Prepare small glass vials. Clean glass vials (~6 ml is a convenient size), being careful to remove any traces of cleaning solution by flushing with plenty of distilled water. Contamination by trace amounts of surfactant can affect results. We soak vials in distilled water in an ultrasonic bath overnight. Dry thoroughly.

- 3.2 Add oil (or oil mixed with 1-MN) to vial. Accurately measure the amount of oil required into the sample vial. If the oil can be delivered by syringe, one strategy is to use a 1-ml glass syringe with 0.01 ml resolution. Parts of the syringe in contact with oil should be either glass or Teflon. If the oil cannot be delivered by syringe, the desired amount can be weighed into the vial and the volume calculated from the density. Larger volumes can be used to increase accuracy if sufficient oil is available.
- 3.3 Add precipitant to the oil. The required amount of n-heptane or other precipitant can be added to the vial using a similar syringe. Note: always add precipitant to oil (add slowly, with plenty of stirring to avoid high local concentrations of precipitant); **never add oil to precipitant!** Adding small volumes of oil to a large volume of precipitant will cause premature precipitation of the asphaltenes. While asphaltenes may, in theory, be stable in the final mixture, prematurely precipitated material may persist much more than the one-day period allotted for these tests.
- 3.4 Seal the vial immediately. A Teflon-lined aluminum cap works well. Precipitants and many of the components of the oil are volatile; evaporation will change the overall composition and invalidate the results of these tests. Shake the vial vigorously until the mixture appears homogeneous. Then allow the mixture to rest at ambient conditions for one day before observation.
- 3.5 Observe asphaltene flocculation. After aging for one day, a few drops of each mixture can be removed from the vial (disposable syringes are useful for this step), deposited on a glass microscope slide, covered with a cover slip, and observed immediately. It is helpful to prefocus the microscope using an old sample in which asphaltenes are obvious that is kept by the microscope for this purpose. Since evaporation begins when the sample is removed from the vial, it is important not to waste time during the actual observation. This is especially problematic with very light oils and highly volatile precipitants such as n-pentane and n-hexane; the accuracy of tests may be questionable if rapid evaporation is a problem. The flocculated asphaltenes usually appear as flowing particles and/or aggregates.
- 3.6 Measure refractive index. An additional sample can be removed from each vial and used to measure RI. An automatic refractometer (Index Instruments, model GPR 11-37) is convenient for this purpose. Temperature should be maintained at 20°C with a circulating water bath. Transfer mixture to the prism surface of refractometer as quickly as possible; seal immediately with the specially designed cap to prevent evaporation. Temperature equilibration requires a few seconds. Record the initial stabilized RI reading. With time, the RI may drift for these mixtures as asphaltenes adsorb and/or deposit on the prism surface, so it is important to take the initial reading.

- 3.7 Testing for the onset with additional precipitants. Once the onset has been found with n-heptane, that result can be used to predict the onset with other alkanes and used to streamline the search strategy for any additional tests. A maximum variation of between 5 and 15% in the amount of precipitant required at onset has been found for n-alkanes from pentane to pentadecane. For more information on the relationship between alkane molecular size and the onset conditions, refer to the references below.

References

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