

Fuel, Energy, and Petrochemical Analysis

Using Automated Flocculation Titrimetry to Reduce Fouling from Heat-Induced Deposition and Coking

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Background Information

Flocculation is a process in which flocs are formed by clustering together particles that are suspended in fluids and mixtures. These flocs are usually formed with an addition of a chemical called flocculants. This process is commonly used and known for cleaning and filtering dirty, contaminated water to make drinkable, clean water as seen in Figure 1.



Fig. 1 Flocculants added to turbid water coagulate unwanted particles.¹

In the petrochemical industry, mixing high- and low-grade crude oils is important to reach target specifications while using the minimal amount of high-grade crude oil. However, as seen in Figure 2, mixing incompatible oils can cause asphaltene precipitation. Polar asphaltene is suspended in crude oil, which has a lower polarity, by resins that have intermediate polarity. These suspensions can be deconstructed irreversibly by pyrolysis as the solvent is heated over 340 °C.

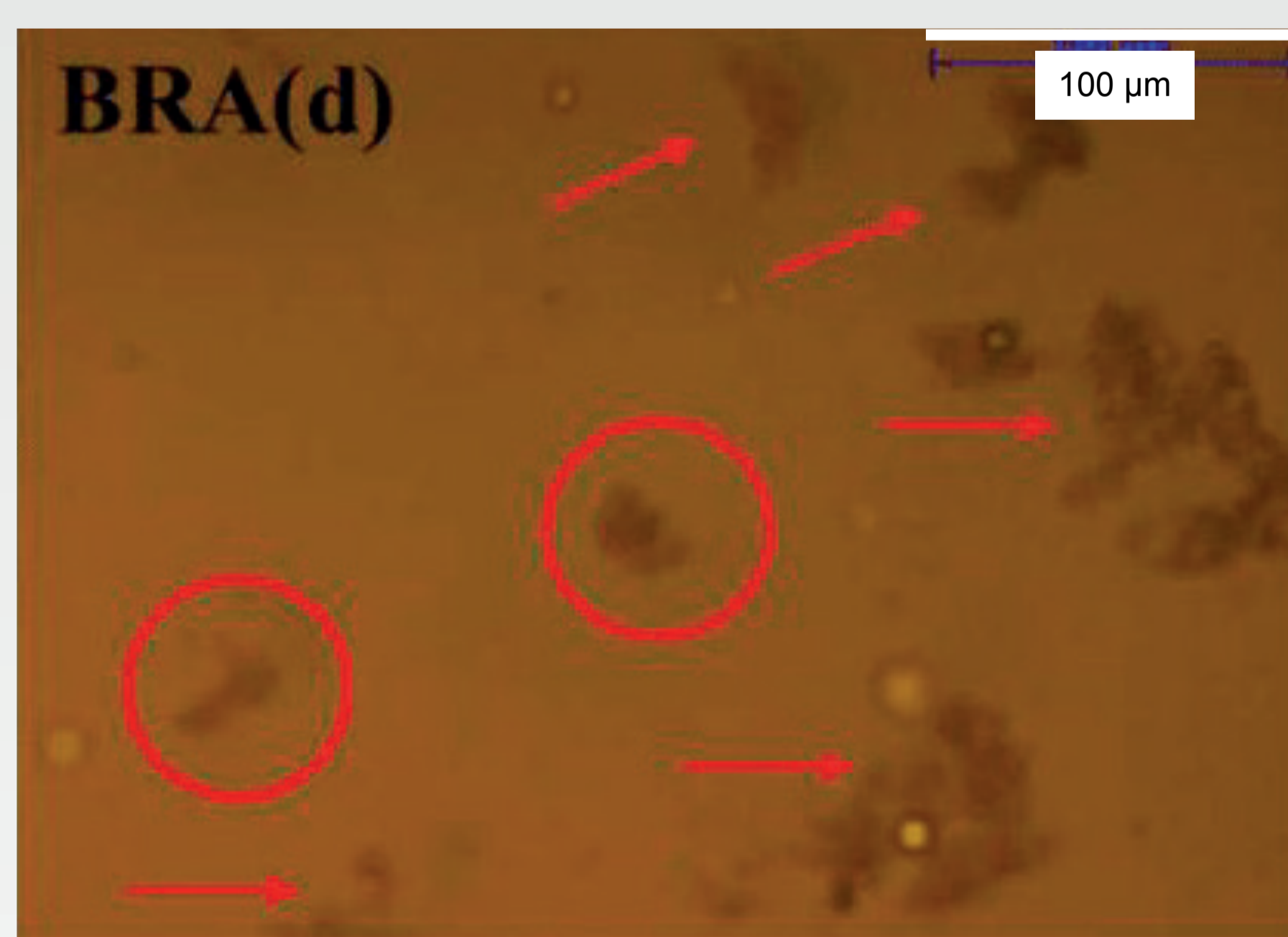


Fig. 2 Crude oil blend of B, R, and A with a n-heptane volume fraction of 0.75.²

Methods

The Automated Flocculation Titrimeter, or AFT, seen below, is a useful tool to predict when coking and heat-induced fouling will occur and determine whether heavy oils are compatible for mixing.



Fig. 3 Automated Flocculation Titrimeter Model K47100/K47190.

First, the AFT is loaded with an oil-toluene mixture highlighted in blue in Figure 4. Iso-octane is used to titrate the toluene solutions in sealed vials. The vials are kept in heating/cooling baths (maroon) to allow for temperature control, and a magnetic stirrer (green) inside the vials ensure homogeneity. The solutions are circulated through a flow quartz cell (yellow) that is connected to a spectrometer. The end point, referred to as the flocculation onset point, is detected as a decrease in transmittance at 740 nm due to scattering from the flocculation of asphaltenes.

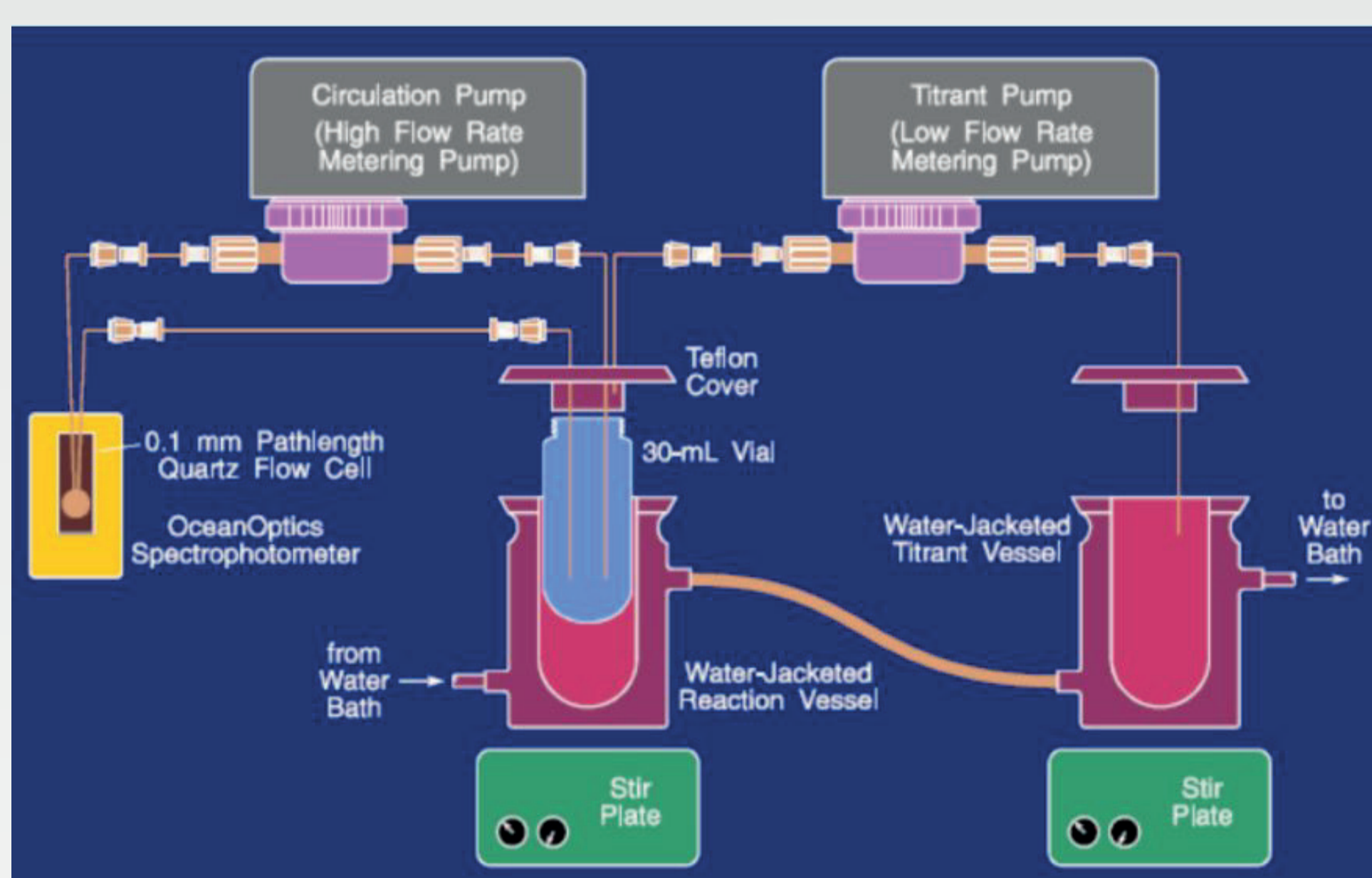


Fig. 4 ASTM D6703, the standard test method for Automated Heithaus Titrimetry

Data Collection

The FR vs C graph below generated by the AFT helps us determine the asphaltene peptizability parameter also known as pa. This parameter is used to calculate the WRI Coking Index Parameter along with the X-intercept of the graph. The WRI Coking Index Parameter is an indicator that shows the proximity to coke formation. As the residuum is pyrolyzed, the WRI parameter decreases, and when the value goes below 0.2, coke is formed.

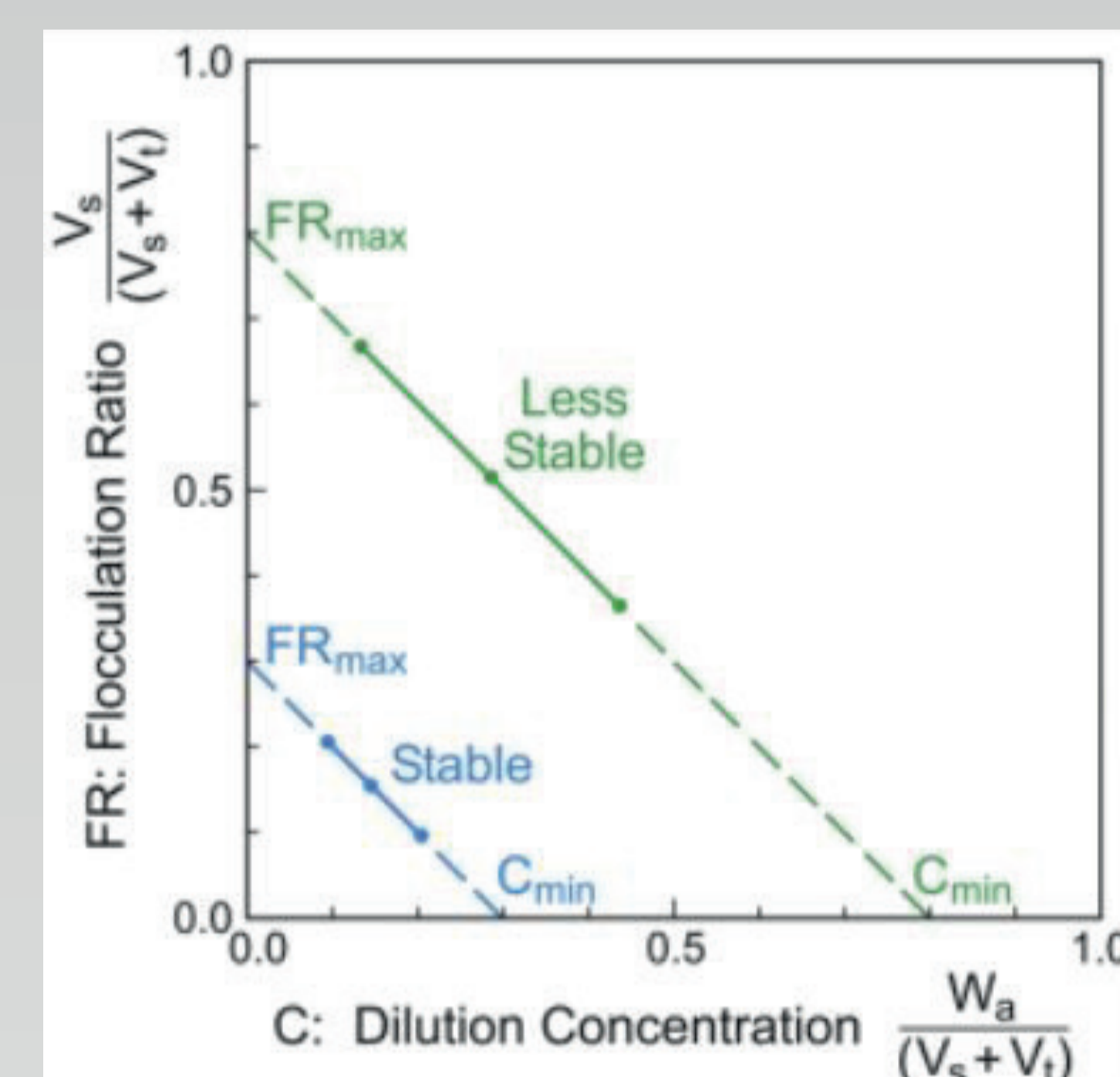


Fig. 5 Flocculation ratio vs Dilution concentration graph made from data collected by the AFT.

Conclusion

The AFT measures the state of the dispersed particle system and calculates predictive parameters for heavy oils. It can also be used to provide valuable information about the internal stability of heavy oils, the proximity of a pyrolyzed oil to coke formation, and to design blending protocols for oils mixtures to prevent asphaltene precipitation.

Sources

1. Chemical Coagulants Used in Water Treatment. [SNF] <https://www.snf.co.uk/chemical-coagulants-used-water-treatment/>
2. Santos, D.; Filho, E.B.M.; Dourado, R.S.; et. al. "Study of Asphaltene Precipitation in Crude Oils at Desalter Conditions by Near-Infrared Spectroscopy." *Energy & Fuels*. 2017, 31(5), 5031-5036.

Acknowledgements

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