



New method of estimating the continuous solubility curve of asphaltenes in crude oils under various pressure and temperature conditions

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Abstract

Currently, laboratory tests are being performed under pressure on samples for which there is a risk of solid layer formation on the inner wall of the pipes. These tests aim to determine an "asphaltene onset pressure" parameter commonly referred to as AOP, i.e. the pressure below which micrometer sized aggregated solid asphaltene particles can be observed in suspension in the oil. AOP is usually assumed to be the pressure corresponding to the appearance of problems related to the accumulation of asphaltenes on the walls. The immediate subsequent industrial question is related to the cleaning frequencies. The estimation of asphaltenes deposition rates requires the use of mass transfer models, where the aggregation, convection and diffusion equations are solved. Thus, the unstable asphaltenes concentration or precipitation curve is a crucial input to such models.

However, its direct measurement by physical separation methods at field conditions faces practical difficulties. This study proposes a new method for estimating asphaltene solubility curves in live crude oil samples.

Keywords

Asphaltenes; Deposition;

Introduction

The "primary" unstable asphaltenes refer to the asphaltene components that first lose their stability and form aggregates with other asphaltene components, which aggregates may grow further and/or settle on pipe walls. The primary unstable asphaltenes are considered as the predominant contributors to deposition on contacted solid surfaces under flowing conditions, as a function of time.

Methodology

A closed stirred-batch reactor is introduced to measure asphaltenes deposition during the continuous titration of n-heptane in an initial volume of crude oil. The apparatus consists of an immersed sensor in a center-position of the reactor.

The presented method consists in the following steps:

a) causing the oil sample to flow on a sensing device ; the one used in this study is an immersed piezoelectric resonator capable of sensing mass accumulation as low as tens of nanograms while varying parameters. The set-up is presented in the following schematic:

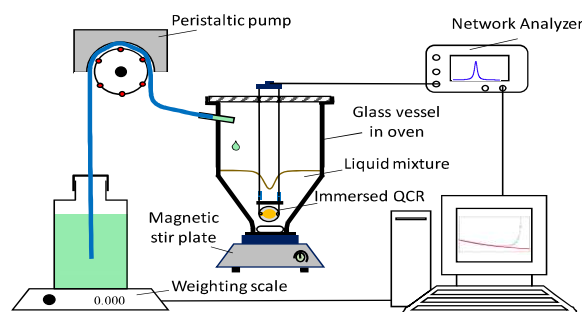


Figure 1. Used experimental set-up at atmospheric pressure

b) varying at a least one parameter among temperature of the oil sample, pressure and amount of precipitant component added to the oil sample;

c) measuring a mass of asphaltenes deposited on the sensing device while at a least one parameter varies; and

d) calculating a concentration of unstable asphaltenes from the measured deposition rate of asphaltenes and a diffusion coefficient of primary unstable asphaltenes present in the oil sample, estimated based on a hydrodynamic radius of the primary unstable asphaltenes.

Results and Discussion

The sensitivity of the used sensor allows to study mass transport of species from the fluid environment toward solid surfaces of the resonator at multiple conditions using limited experimental volumes.

The mass of deposited asphaltenes on the sensor is recorded while changing conditions, e. g. Figure 2 show the deposited mass of asphaltenes as a function of time during n-heptane continuous addition. The diffusion-limited model is used to match experimental data by adjusting D_A , the diffusion coefficient of contributing asphaltenes to the deposit build-up.

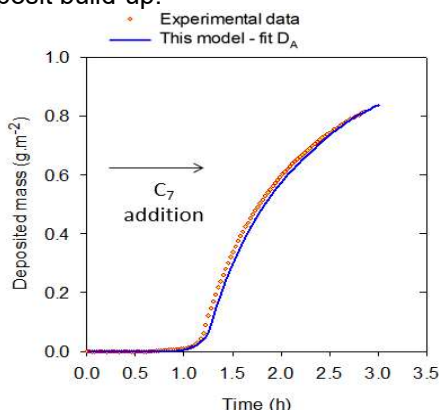


Figure 2. Deposited mass as a function of time during n-heptane titration of a crude oil at atmospheric pressure

Theoretical relationships between concentration and deposition rate under Stokes flow let us relate the amount of destabilized asphaltenes in the surrounding bulk to the deposited mass on the sensor, as illustrated in Figure 3.

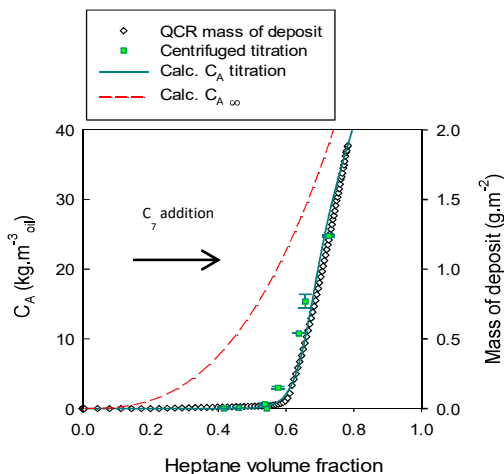


Figure 3. **Cumulative** deposited mass, concentration of unstable asphaltenes at equilibrium $C_{A\infty}$ and instantaneous concentration of unstable asphaltenes C_A as a function of n-heptane volume fraction during n-heptane titration of a crude oil at atmospheric pressure

Using a unique titration while recording the deposited asphaltenes on the sensor therefore allows backcalculating the solubility profile of asphaltenes of a crude oil at studied conditions.

Results obtained with the present method are compared to physical separation of particles > 0.2 micrometer by centrifuge methods, as showed in Figure 4.

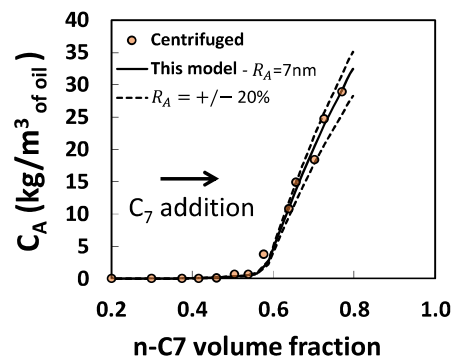


Figure 4. Concentration C_A of unstable asphaltenes vs n-heptane fraction in oil-heptane mixture during continuous heptane addition

The method allows to estimate the concentration of unstable asphaltenes or solubility profile of asphaltenes of crude oil by performing a continuous and single experiment requiring limited volumes of samples. It applies to investigate the effect of pressure, temperature, and any alkane addition on asphaltenes solubility curves. The rate of asphaltenes deposition in oil conduits is subsequently calculated.

Results of this research also open the possibility to study the thermodynamic modeling of asphaltenes under conditions of the upstream and the downstream industry.

Conclusions

Results show that the deposition rate of unstable asphaltenes scales with the square root of the fluid flow velocity. Asphaltenes accumulation on solid surfaces of the sensor can then be explained by a diffusion-limited phenomenon involving nanoparticles. The average hydrodynamic radius R_A of depositing units generally ranges between 1 nm and 10 nm. The deposition rate of asphaltenes scales linearly with the calculated concentration of primary particles at $C_1(t)$. The asphaltene deposition rate accordingly develop into a strong dependence on the rate of change of the liquid composition, as expected. The presented method [1] is successfully applied to a case of crude oil-heptane mixture.

Therefore, the method, which is based on the track the deposited mass of asphaltenes can indirectly quantify bulk solubility curve of asphaltenes.

Acknowledgments

I wish to dedicate this paper to Prof. Fogler who dedicated his life to science and who will remain in our memory.

Responsibility Notice

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