

Development of an Asphaltene Deposit Cleaning Technology Using a QCMB Technique

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ABSTRACT

Asphaltenes are a components of crude oil defined as a solubility class, i.e., as a component of crude oil insoluble in n-pentane (C5 asphaltenes) or n-heptane (C7 asphaltenes) but soluble in aromatic solvents such as toluene, and are complex, polyaromatic, macrocyclic structures with an overall varied composition. Asphaltene deposition, remediation, and inhibition are important considerations for flow assurance in upstream processes, but methodologies to assess performance for cleaning purposes can provide variable results. We report on the development of a dispersant additive for aromatic solvent systems using a QCMB technique for evaluating the cleaning of a deposit. Further, we report the performance of the additive in a case study and, hence, the utility of the technique to provide an assessment for potential field use.

Keywords: asphaltenes, dispersants, quartz crystal microbalance

INTRODUCTION

Asphaltenes are a component of crude oil defined as a solubility class, i.e., as a component of crude oil insoluble in n-pentane (C5 asphaltenes) or n-heptane (C7 asphaltenes) but soluble in aromatic solvents such as toluene, that exist as black, shiny, friable solids. Asphaltenes are complex, polyaromatic, macrocyclic structures with an overall varied composition, containing not only carbon (C), oxygen (O), sulfur (S), and nitrogen (N), but also small amounts of transition metals, primarily consisting of nickel (Ni), vanadium (V), and iron (Fe) ligated complexes. These large, overall “flat” molecules have molecular

weights typically at 750 Daltons (g/mol) and in the range of 300 – 1,400 Daltons, but readily form larger aggregates that can deposit to block reservoir pores near a wellbore, in production tubing, and in downstream pipelines and processing facilities. The lower molecular weight range is typically part of the C5 asphaltene fraction, whereas a C7 asphaltene may exclude these smaller asphaltenes. Overall, asphaltene deposition, remediation, and inhibition are important considerations for both upstream and downstream processes.

Crude oil (dead oil, or oil that has lost its gaseous components) is typically characterized in terms of its composition of saturates, aromatics, resins, and asphaltenes (SARA) via laboratory methods for such general fractionation.¹ Correspondingly, asphaltenes are the components of crude oil that are insoluble in n-alkanes such as pentane or heptane but soluble in aromatic hydrocarbons such as toluene or xylenes.² A wide range of techniques have been used to study asphaltenes in attempts to characterize them chemically and structurally as part of the overall field of petroleomics. Analytical methods include mass spectrometry, electron microscopy, nuclear magnetic resonance, small-angle neutron and X-ray scattering, ultrasonic spectroscopy, multi-angle dynamic light scattering, fluorescence correlation spectroscopy, fluorescence depolarization, vapor-pressure osmometry, and gel permeation chromatography.^{3,4,5,6,7,8,9,10,11} Overall, mass spectrometry and molecular diffusion experiments have produced the most consistent data for the estimation of asphaltene molecular weight and size. This has provided the scientific foundation for further understanding of how asphaltene stability within a crude oil is perturbed and potential means of both preventing and remediating the issues associated with their deposition.

Precipitation and deposition may be caused by a variety of conditions, including changes in pressure, temperature, shear rate, and even composition of the production fluids. These changes are affected and induced by a range of factors, including primary depletion, injection of natural gas or CO₂, acidizing treatments, and commingled production of incompatible fluids. Each of these has the potential of destabilizing the asphaltene dispersions in a given crude oil. A general view of asphaltene stability as a function of both pressure and temperature ($f(P,T)$) has arisen and been previously reported.¹² However, more recent studies utilizing model systems have indicated that there is a possibility of a minimum in the asphaltene stable region at certain high temperatures and pressures near the bubblepoint.¹³

These factors are understood to contribute to the corresponding potential for deposition which can lead to significant operational issues. In upstream processes, asphaltenes can precipitate and deposit at many points along the production system, such as inside the formation (e.g., the near-wellbore region of the production pipe), deposit and buildup in the wellbore, gunk and deposit in flowlines, generate solids in the separator, as well as pumps, wellheads, safety valves and additional surface facilities. This can lead to reduced production or shut-in downtime.

Consequently, researchers have sought to develop new techniques not only to understand the conditions by which asphaltenes may deposit, but also to evaluate chemistries to either inhibit their precipitation or remediate existing deposits. In the former case, depressurization tests have been used to evaluate inhibitors that are intended to prevent the aggregation of Asphaltene molecules and shift the onset of the flocculation pressure. As the pressure drops during oil production but remains above the bubble point, the density of the oil decreases and the volume fraction of lighter hydrocarbons increases. This reduces the polarity of the oil and initiates asphaltene flocculation. Often this occurs downhole, but can occur anywhere in the system. Determination of the pressure at which deposition occurs at reservoir temperatures can provide insight into the potential for problems downhole.¹⁴ Product performance can be ranked by studying the asphaltene flocculation point determined, although this is most accurately done with a live oil sample – a sample of crude containing volatile gases from production that is typically sampled at downhole temperatures and pressures and kept at or above the pressure / temperature during

transport for laboratory evaluations in specialized equipment.¹⁴ This delay of the onset point of deposition allows for moving asphaltene precipitation out of the wellbore to a point in the production system where it can be dealt with much more easily. Hence, inhibition is not complete inhibition but a delay in the kinetics of deposition. Essentially, the inhibitors behave as threshold inhibitors, analogous to polymers in scale deposit control.

However, the challenges and cost of prevention can be sufficiently high that often the most common solution is remediation via periodic batch treatment of dispersant / cleaner chemical packages. Dispersant chemistries do not affect the onset point of asphaltene flocculation but are able to keep asphaltenes suspending in the crude oil, by reducing particle size and maintaining intermolecular repulsive forces (i.e., impacting particle zeta potential). Dispersant chemistries are typically non-polymeric surfactants. Dissolvers are typically solvents or solvent packages that are batch treated to remove asphaltene deposits.

Techniques to evaluate the performance of dispersants have focused methods whereby the settling rate of isolated, dispersed asphaltene particles are compared.^{15,16} These tests correspond to a prevention strategy, though, focusing on keeping precipitated asphaltenes suspended vs a remediation strategy of cleaning a deposit. In a remediation scenario, simple dissolution tests are used whereby the amount of deposit dissolved is measured either via the mass of the collected, undissolved material or via spectrophotometric analysis as compared to a standard curve created from the deposit. These methods tend to have a wide variance in the experimental results. Ultimately, this proves to be challenging for lab scale determination of the relative performance of different solvent and dispersant packages under consideration for remediation protocols.¹⁷

In this regard, we have developed a methodology utilizing a quartz crystal microbalance (QCMB) to evaluate the ability of solvents and dispersant additive technologies to remove Asphaltene deposits from a surface. This novel modification of the technique has shown differences in performance of solvents to dissolve and remove asphaltene deposits from a surface with and without additives, leading to development of technologies for field evaluation. Further, the general improvement measure using this lab technique was shown to translate to field performance in a corresponding field trial.

EXPERIMENTAL PROCEDURE

Test System

A flow loop was constructed utilizing a quartz crystal microbalance flow cell connected to a reciprocating piston pump and appropriate sized tubing to provide plug flow within the system. A Gamry™ eQCM 10M oscillator was used along with a Gamry™ 600 potentiostat. Solvent and chemical packages were injected into the system via an auto injector module at defined intervals. Asphaltene deposits were used as received from the field. The samples were initially dissolved in solvent, then the solution applied to the QCM and dried. The targeted quantity was confirmed with control runs via multiple solvent injections to ensure complete removal of the deposit.

A baseline acquisition is acquired at the start of the experiment, with the resulting mass loss determined following injection of sample. Typically, approximately 70 micrograms of the field deposit was applied to the crystal. Care must be taken to be sure the crystal surface is centered in the flow through cell for accurate measurements.