



Characterization of Interfacial Material from Fractionated Athabasca Bitumen by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Introduction

Emulsions are an important part of steam-assisted gravity drainage (SAGD) operations for bitumen recovery. In SAGD, steam is injected into the bitumen reservoir, to decrease the viscosity of the bitumen, so that it may flow to the well and be recovered to the surface. However, once bitumen has been recovered, it is necessary to break the emulsion to limit crude oil loss as well as possible corrosion and catalyst deactivation issues. Knowledge of compounds at the oil/water interface can help determine how to best treat an undesirable emulsion formation. Previous studies have suggested that asphaltenes, the *n*-pentane/heptane insoluble fraction, may play the most significant role in stabilizing emulsions within Athabasca bitumen.^{1,2} Here, we will isolate interfacial material (IM) from the soluble and insoluble *n*-pentane and *n*-heptane fractions as well as the whole crude using a novel, wet silica method. Isolated interfacial material will then be characterized by positive atmospheric pressure photoionization (APPI) 9.4 T Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), and emulsion stability testing will be performed to determine which fraction contributes most to emulsion stability observed in the whole crude oil.

Methods

Fractionation of Crude Oil

C-5 maltenes and asphaltenes were isolated from Athabasca bitumen by dissolving 10 g of the whole crude oil in 500 mL of *n*-pentane. The crude oil solution was then refluxed for 1 hour. After reflux, the solution was filtered through a Whatman Grade 2V filter to separate the *n*-pentane soluble fraction (C-5 maltenes) from the insoluble fraction (C-5 asphaltenes). The asphaltenes were then added to a Soxhlet extractor and washed with *n*-pentane for 1 week to remove any maltene carryover. The asphaltenes were then dropped from the filter paper using 500 mL of toluene. This procedure was repeated with *n*-heptane substituted for *n*-pentane to isolate C-7 fractions. All fractions were dried under N₂ gas before further experiments were performed.

Isolation of Interfacial Material

Interfacial material (IM) was isolated by a novel wet silica method³, which generates two fractions. A 5 weight percent solution of crude oil was first dissolved in heptol (1:1 mixture of *n*-heptane:toluene) and added to one gram of wet silica gel (FisherScientific, 100-200 mesh, type 60A). The mixture was shaken by hand to generate a slurry, which was then loaded into a 5 mL borosilicate glass pipet packed with glass wool at the end. The column was then washed with 10 mL of heptol to ensure that all of the unretained compounds that did not interact with the wet silica had been washed off and collected as the first fraction. The compounds retained (IM) on the stationary phase were eluted with 10 mL of 10:25 (v/v) methanol:toluene and collected as the second fraction. All samples were dried under N₂ gas before analysis.

Sample Preparation for FT-ICR MS

All fractionated oil and IM samples were dissolved in toluene to create 1 mg/mL stock solutions. Final samples were further diluted with methanol to 100 µg/mL in 50:50 (v/v) methanol:toluene for (+) APPI 9.4 T FT-ICR MS analysis. Data were calibrated and processed with custom software packages (PREDATOR and PetroOrg, copyright 2012).

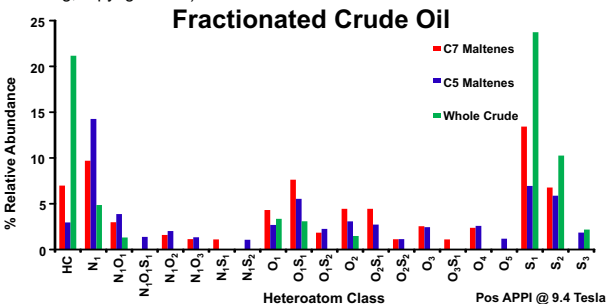


Figure 1. Heteroatom class distribution for Athabasca bitumen whole crude and fractions by (+)APPI 9.4 T FT-ICR MS.

Emulsion Stability Testing

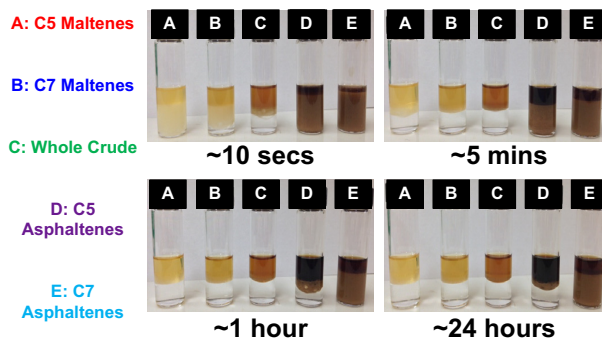


Figure 2. Emulsion stability testing. Two milligrams of each sample were added to a benign system consisting of 2 mL HPLC grade H₂O with NH₄OH solution (28% in H₂O, pH ~11), and 2 mL toluene.

Isolated Interfacial Material

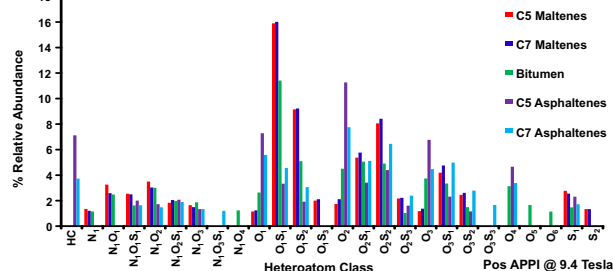


Figure 3. Heteroatom class distribution for Athabasca bitumen IM species isolated from the whole crude and fractionated oil by (+)APPI 9.4 T FT-ICR MS.

Emulsion Stability Testing

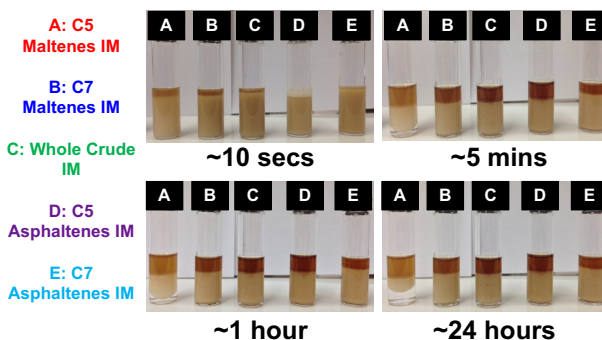


Figure 4. Emulsion stability testing. Two milligrams of each sample were added to a benign system consisting of 2 mL HPLC grade H₂O with NH₄OH solution (28% in H₂O, pH ~11), and 2 mL toluene.

Select Oxygen Species in Isolated Interfacial Material

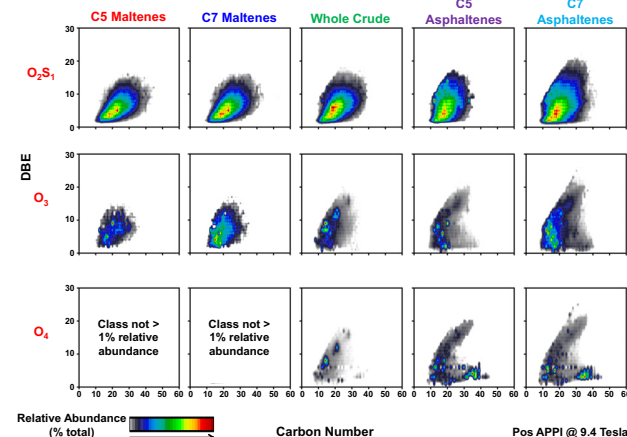


Figure 5. Positive APPI derived isoabundance-contoured plots of double bond equivalents (DBE = rings plus double bonds to carbon) vs. carbon number for the O₂S₁ (1st row), O₃ (2nd row), and O₄ (3rd row) classes of interfacial material isolated from C-5 maltenes (1st column), C-7 maltenes (2nd column), whole Athabasca bitumen (3rd column), C-5 asphaltenes (4th column), and C-7 asphaltenes (5th column).

Conclusions

While previous studies have suggested that asphaltenes play the most significant role in emulsion stabilization^{1,2}, these results show that IM isolated from Athabasca bitumen contains both maltenic and asphaltenic material. Emulsion stability testing with the whole crude and fractionated oil reveals that the asphaltene fractions form the most stable emulsions in bitumen. These asphaltene fractions are enriched in polar species relative to the maltene fractions and whole crude oil. However, when IM species are isolated with the wet silica method, compositionally similar polar, IM species are isolated from each fraction. Emulsion stability testing with IM from each fraction reveals that IM from all fractions forms a stable emulsion. Comparison of class specific isoabundance-contoured plots of double bond equivalent (DBE = number of rings + double bonds to carbon) versus carbon number displays that IM isolated from the whole crude oil has a higher DBE range relative to the maltene fraction. This suggests that IM isolated with the whole crude oil contains both maltenic and asphaltenic material. Future work will include critical electric field (CEF) testing on IM fractions to quantitatively determine emulsion stability.

Acknowledgments

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