

**ASPHALTENE PRECIPITATION STUDIES: MODELING, VALIDATION,
AND PREVENTION**



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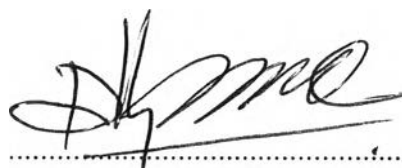
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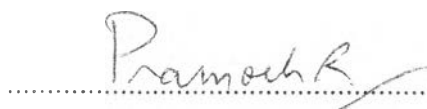
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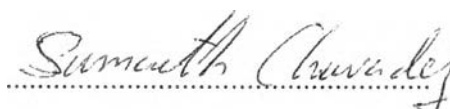
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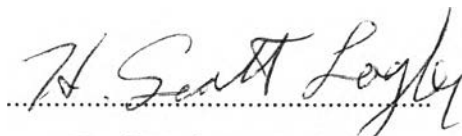
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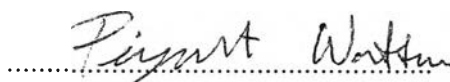
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ABSTRACT

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Prevention/ Solubility Parameter/ Validation

Asphaltene precipitation and deposition caused by changes in composition, pressure, and temperature during oil production have a huge economic impact in the oil industry because of production losses and high remediation costs. To better understand and better predict asphaltene precipitation, different models for asphaltene precipitation were investigated and a thermodynamic model has been developed to predict asphaltene precipitation onset conditions from ambient titration data. The model predictions were validated using high pressure – high temperature titration and pressure depletion experiments.

When asphaltene precipitation can not be avoided during oil production, asphaltene dispersants are used to prevent asphaltenes from flocculating into large particles and depositing onto the pipe wall. Asphaltene dispersants were investigated using a variety of measurement techniques (automated flocculation titrimeter, optical microscope, turbidity measurement device, and particle size distribution measurement device). The results show that asphaltenes in stable crude oil are nanoaggregates (less than 20 nm). However, when destabilized, these nanoaggregates agglomerate and form larger particles of the size greater than 1 micron, which can settle and deposit. Asphaltene dispersants can stabilize asphaltenes by preventing them from growing larger than 1 micron and thus delay the settling.

บทคัดย่อ

เกรียงไกร ไกรวัฒนวงศ์ : การศึกษาการตกตะกอนของแอสฟัลทีน การออกแบบ
รับรองผล และการป้องกัน (Asphaltene Precipitation Studies: Modeling, Validation, and
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การตกตะกอนและการสะสมของแอสฟัลทีนเนื่องจากการเปลี่ยนแปลงของส่วนประ-
กอบ ความดัน และอุณหภูมิ ระหว่างการผลิตน้ำมันมีผลกระทบอย่างมากสำหรับอุตสาหกรรม
น้ำมัน เพราะการสูญเสียทางการผลิต และรายจ่ายในการแก้ไขที่สูง เพื่อความเข้าใจและการทำนาย
การตกตะกอนของแอสฟัลทีนที่ดีขึ้น แบบจำลองต่างๆของการตกตะกอนของแอสฟัลทีน ได้ถูก
สำรวจ และแบบจำลองทางเทอร์โมไดนามิกได้ถูกพัฒนาขึ้นเพื่อทำนายสภาวะตกตะกอนของ
แอสฟัลทีนจากของมูลที่สภาวะปกติ การทำนายของแบบจำลองได้ถูกรับรองโดยการทดลอง
ไทเทรตที่ความดันสูง-อุณหภูมิสูงและการทดลองลดความดัน

เมื่อการตกตะกอนของแอสฟัลทีนไม่สามารถหลีกเลี่ยงได้ระหว่างการผลิตน้ำมัน สารที่
ทำให้แอสฟัลทีนแพร่กระจายถูกใช้เพื่อป้องกันแอสฟัลทีนจากการรวมตัวเป็นอนุภาคใหญ่ และ
สะสมที่ผนังท่อ สารที่ทำให้แอสฟัลทีนแพร่กระจายถูกสำรวจโดยใช้การวิเคราะห์ต่างๆ (การ
ไทเทรตอัตโนมัติ กล้องจุลภาคน์ อุปกรณ์วัดความขุ่น และอุปกรณ์วัดการกระจายตัวของอนุภาค)
ผลการทดลองแสดงให้เห็นว่าแอสฟัลทีนในน้ำมันดิบที่มีเสถียรภาพเป็นกลุ่มก้อนขนาดเล็ก (เล็ก
กว่า ๒๐ นาโนเมตร) อย่างไรก็ดีเมื่อถูกทำให้เสถียรภาพกลุ่มก้อนขนาดเล็กเหล่านี้รวมตัวกัน
เป็นอนุภาคขนาดใหญ่ขึ้นและมีขนาดใหญ่กว่า ๑ ไมครอนซึ่งสามารถนอนกันและสะสมได้ สารที่
ทำให้แอสฟัลทีนแพร่กระจายสามารถสร้างเสถียรภาพ โดยการป้องกันไม่ให้กลุ่มก้อนเหล่านี้
รวมตัวกันใหญ่เกินกว่า ๑ ไมครอน และดังนั้นทำให้การนอนกันช้าลง

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ABBREVIATIONS

AFT	Automated Flocculation Titrimeter
ASM	Asphaltene Solubility Model
DBSA	4-Dodecyl Benzene Sulfonic Acid
DG	Dissolved Gas
DP	4-Dodecyl Phenol
DR	4-Dodecyl Resorcinol
EOS	Equation of State
ESI-FT-ICR-MS	Electron Spray Ionization – Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy
FIMS	Field-Ionization Mass Spectroscopy
FWHM	Full-Width Half Maximum
H/C	Hydrogen/Carbon
HRTEM	High-Resolution Transmission Electron Microscopy
MI	Miscible Injectant
mL	milliliter
NIR	Near Infrared
nm	nanometer
ppm	part-per-million
psi	pound per square inch
psia	pound per square inch absolute
psig	pound per square inch gauge
PSD	Particle Size Distribution
SARA	Saturates, Aromatics, Resins, and Asphaltenes
SFC	Supercritical Fluid Chromatography
SOP	Standard Operating Procedure
STM	Scanning Tunneling Microscopy
STO	Stock Tank Oil
TRFD	Time-Resolved Fluorescence Depolarization
VLE	Vapor-Liquid Equilibrium

LIST OF SYMBOLS

α	Temperature correction factor (-)
C_{pen}	Peneloux molar volume correction (cm ³ /mol)
C_R	Resin concentration (g/mL)
$(C_R)_{crit}$	Critical resin concentration (g/mL)
D	Ratio of live oil volume to stock tank oil volume under reservoir conditions (-)
δ	Solubility parameter (MPa ^{1/2})
δ_a	Solubility parameter of asphaltenes (MPa ^{1/2})
δ_{DG}^M	Molar solubility parameter of the dissolved gas (MPa ^{1/2} mL/mol)
δ_{DG}^{RC}	Solubility parameter of dissolved gases under reservoir conditions (MPa ^{1/2})
δ_i	Solubility parameter of component i th (MPa ^{1/2})
δ_i^M	Molar solubility parameter of i th component (MPa ^{1/2} mL/mol)
δ_L	Solubility parameter of crude oil (MPa ^{1/2})
$\delta_{LiveOil}$	Solubility parameter of live oil (MPa ^{1/2})
δ_m	Solubility parameter of maltenes (MPa ^{1/2})
δ_{mix}^M	Molar solubility parameter of the mixture (MPa ^{1/2} mL/mol)
$\delta_{mixture}$	Solubility parameter of a mixture (MPa ^{1/2})
δ_o	Solubility parameter of crude oil (MPa ^{1/2})
δ_{onset}	Onset solubility parameter (MPa ^{1/2})
δ_p	Solubility parameter of precipitant (MPa ^{1/2})
δ_s	Solubility parameter of solvent (MPa ^{1/2})
δ_{STO}	Solubility parameter of stock tank oil (MPa ^{1/2})
δ_{STO}^{RC}	Solubility parameter of stock tank oil under reservoir conditions (MPa ^{1/2})
ΔG_{mix}	Gibbs free energy of mixing (J)

ΔH^{vap}	Heat of vaporization of the liquid (J/mol)
ΔU^{vap}	Energy of vaporization to the gas at zero pressure (J/mol)
ϕ_a^*	Volume fraction of asphaltenes in the nucleating phase at the onset point (-)
$(\phi_a)_{max}$	Maximum volume fraction of asphaltenes soluble in crude oil (-)
ϕ_{DG}^{RC}	Volume fraction of dissolved gases under reservoir condition (-)
ϕ_i	Volume fraction of i^{th} component (-)
ϕ_{STO}^{RC}	Volume fraction of stock tank oil under reservoir conditions (-)
P_c	Critical Pressure (psig)
v	Molar volume of the liquid (cm^3/mol)
v_a	Molar volumes of asphaltenes (cm^3/mol)
v_L	Molar volumes of crude oil (cm^3/mol)
v_m	Molar volumes of maltenes (cm^3/mol)
v_{mix}	Molar volumes of mixture (cm^3/mol)
v_p	Molar volumes of precipitant (cm^3/mol)
v_s	Molar volumes of solvent (cm^3/mol)
v_{STO}	Molar volume of stock tank oil under ambient conditions (mL/mol)
v_{STO}^{RC}	Molar volume of stock tank oil under reservoir conditions (mL/mol)
r	Moles of the dissolved gas per volume of stock tank oil under reservoir conditions (mol/mL)
R	Ideal gas constant (8.314 J/mol/K)
T	Temperature (K)
T_c	Critical temperature ($^{\circ}C$)
V_c	Critical Volume (cm^3/mol)
V_o	Volume of crude oil (mL)
V_p	Volume of precipitant (mL)

V_s	Volume of solvent (mL)
x_i	Mole fraction of i^{th} component (-)