Asphaltenes—Problematic but Rich in Potential

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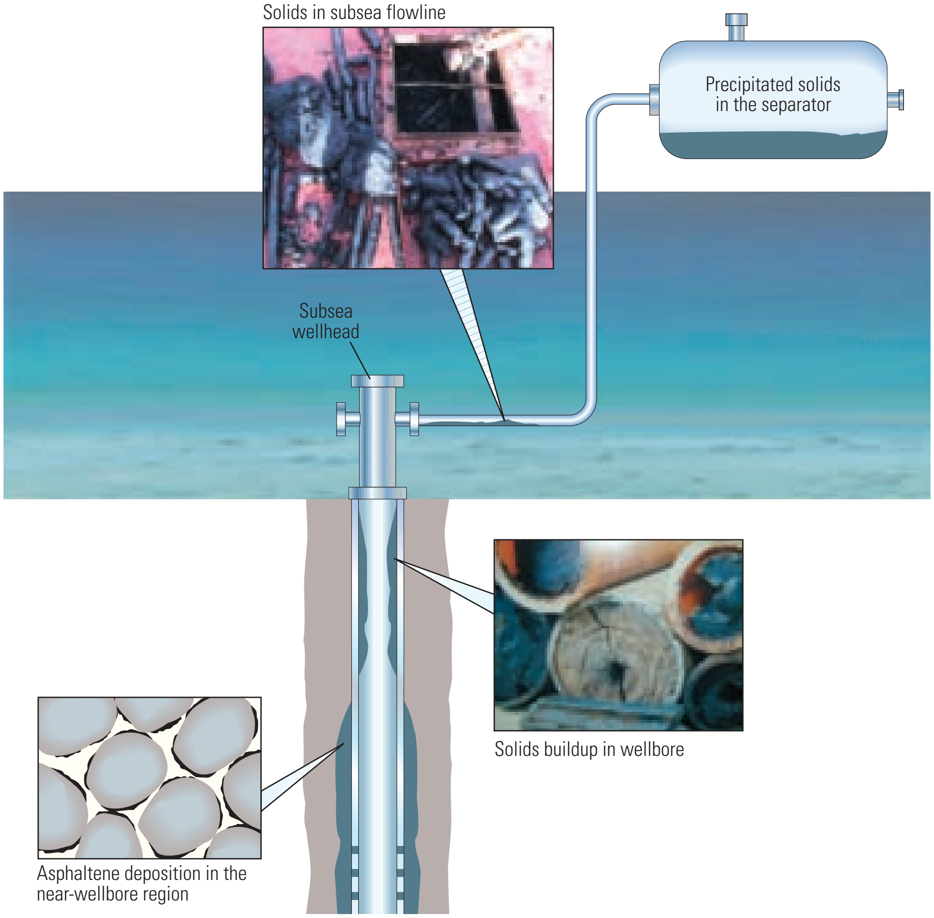
In the oil field, asphaltenes are best known for clogging wells, flowlines, surface facilities and subsurface formations. Laboratory analysis and field intervention help producers avoid or remediate asphaltene deposition. New science is finding ways to use these enigmatic hydrocarbon compounds to better understand reservoir architecture.



^ Asphaltene precipitation and deposition. Changes in pressure, temperature, composition and shear rate may cause asphaltene precipitation and deposition. These changes may be induced by a variety of processes, including primary depletion, injection of natural gas or carbon dioxide, acidizing treatments and commingled production of incompatible fluids. Asphaltenes may build up at many places along the production system, from inside the formation to pumps, tubing, wellheads, safety valves, flowlines and surface facilities.

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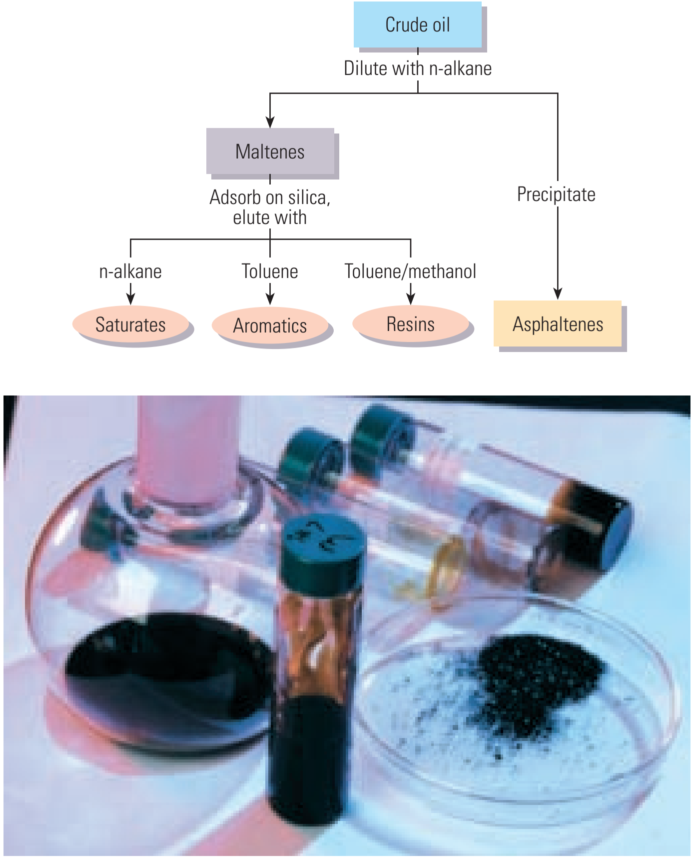
Fluid-property variations that commonly occur during the production of oil, such as changes in pressure, temperature and composition, can precipitate asphaltenes. Small amounts of asphaltenes may adhere to formation grains, pumps, tubulars, safety valves and flowlines without disrupting flow, but thick deposits can bring production to a halt.[1] Optimizing production in this case requires knowing the oil composition and the conditions under which its asphaltenes will remain in solution.

The mere presence of asphaltenes in a crude oil does not portend asphaltene-related production problems. Heavy oils, those with the greatest asphaltene concentrations, are usually stable during production, and do not promote well clogging. Asphaltene-precipitation problems are more common in lighter oils that contain minor amounts of asphaltenes in reservoirs that are at pressures well above bubblepoint.

While asphaltenes have practical uses, such as material for road construction, waterproofing and roofing, and as curing agents and corrosion inhibitors, they are usually considered a menace in the oil field. The potential for asphaltenes to clog systems continues downstream, and is a concern for refiners, because asphaltenes are significant constituents of the heavy oils that are increasingly entering refinery processing streams. Asphaltenes also play a role in the stability of oil-water emulsions, and in formation wettability.

This article first defines asphaltenes and then focuses on their behavior through case studies in upstream environments. We describe laboratory and modeling techniques for predicting the conditions under which asphaltenes will precipitate during production. Then we examine remediation techniques applied when deposition cannot be avoided. We also discuss how asphaltenes are being used to understand reservoir architecture.



Separating crude oil into saturates, aromatics, resins and asphaltenes (SARA). In SARA fractionation (*top*), asphaltenes are separated from the other hydrocarbon components by adding an n-alkane such as n-heptane or propane. The remaining components, called maltenes, are then further fractionated by passing the mixture through a column. Each component is removed from the column by flushing with various solvents. Saturated hydrocarbons, or saturates, are removed by flushing with n-alkane. Saturated means the molecule contains the maximum number of hydrogen atoms possible, with no double or triple bonds between the carbon and hydrogen atoms. Saturates are also called alkanes. The simplest such molecule is methane, [CH_4]. Aromatics incorporate one or more rings of six carbon atoms and six hydrogen atoms. The simplest aromatic is benzene [C_6H_6]. Resins are a solubility class, and somewhat similar to asphaltenes. They are the nonvolatile polar component of crude oil that is soluble in n-alkanes and insoluble in liquid propane.

What Are Asphaltenes?

Asphaltenes are a class of components of hydrocarbons.[2] Naturally occurring hydrocarbon fluids are compounds that span a continuum of composition from dry natural gas to tar. Across that range, density and viscosity increase dramatically, and color changes from clear to deep brown as asphaltene content increases from 0 to nearly 20%.

Certain properties of asphaltenes have been known since before the first commercial oil wells were drilled. The term originated in 1837 when J.B. Boussingault defined asphaltenes as the residue of the distillation of bitumen: insoluble in alcohol and soluble in turpentine.[3] The definition in use today is similar: insoluble in n-alkanes, such as n-pentane or n-heptane, and soluble in toluene. Asphaltenes obtained in this way are dark-colored, friable solids with a density of about 1.2 g/cm^3. They are also infusible, meaning they have no defined melting point, but decompose when heated, leaving a carbonaceous residue.

Because asphaltene content is an important factor in determining the processing and refining paths of a crude oil, a convenient laboratory method has been developed to quantify the asphaltene fraction. This technique separates dead oil, or oil that has lost its gaseous components, into saturates, aromatics, resins and asphaltenes (SARA) depending on their solubility and polarity (above).

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1. Amin A, Riding M, Shepler R, Smedstad E and Ratulowski J: "Subsea Development from Pore to Process," *Oilfield Review* 17, no. 1 (Spring 2005): 4–17.
2. Mullins OC, Sheu EY, Hammami A and Marshall AG (eds): *Asphaltenes, Heavy Oils and Petroelomics*. New York City: Springer, 2007.

   Mullins OC and Sheu EY (eds): *Structures and Dynamics of Asphaltenes*. New York City: Plenum, 1998.

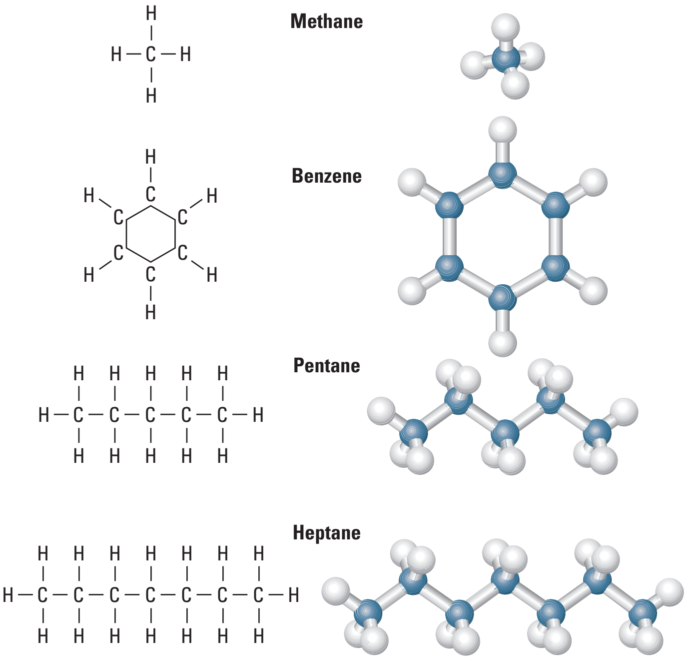
   Chilingarian GV and Yen TF: *Bitumens, Asphalts, and Tar Sands*. New York City: Elsevier Scientific Publishing Co., 1978.
3. Boussingault JB : "Memoire sur la composition des bitumens," *Annales de Chimie et de Physique* 64 (1837): 141. Cited in Auflem IH: "Influence of Asphaltene Aggregation and Pressure on Crude Oil Emulsion Stability," Doktor Ingeniør Thesis, Norwegian University of Science and Technology, Trondheim, June 2002.

The advantage of the SARA method is that it is a simple procedure that can be performed in many laboratories. However, SARA analysis also has several disadvantages that become apparent when it is used for purposes beyond its original intent. First, dead oil lacks the gaseous components that are dissolved in live oils, and so the results are not representative of how the oil would act under reservoir conditions. In addition, laboratory methods vary greatly, and solubility of asphaltenes varies with the type of n-alkane used to precipitate them. This means that a single oil could have two or more SARA results depending on the precipitant used. Because of its simplicity, SARA analysis has become a widespread means for comparing oils, but often, because variations in laboratory technique are not reported, comparisons between laboratories may not be valid. Although the SARA method is a reasonable first step for categorizing dead crude oils, it provides insufficient characterization for both downstream, refining needs and for upstream concerns, where live-oil properties are needed.

The definition of asphaltenes as a solubility class rather than as a chemical class has made them more difficult to study than lighter components. The lighter components of hydrocarbons—saturates and some aromatics—have concisely defined chemical structures (below). However, the heavier components, asphaltenes and their related compounds, resins, have often been lumped together as residue and deemed unworthy of or too challenging for further examination.

While their chemical structure has been slow to come to light, the average composition of asphaltenes as a class is fairly well-known. Elemental analysis shows they are composed of carbon and hydrogen in an approximate 1 to 1.2 ratio, compared with the 1 to 2 ratio for bulk alkanes. Unlike most hydrocarbon constituents, asphaltenes typically contain a few percent of other atoms, called heteroatoms, such as sulfur, nitrogen, oxygen, vanadium and nickel. As far as asphaltene structure is concerned, experts agree that some of the carbon and hydrogen atoms are bound in ring-like, aromatic groups, which also contain the heteroatoms. Alkane chains and cyclic alkanes contain the rest of the carbon and hydrogen atoms and are linked to the ring groups. Within this framework, asphaltenes exhibit a range of molecular weight and composition. This compositional characterization is accepted by nearly all asphaltene specialists, but leaves ample room for debate about the structure or size of individual asphaltene molecules.

The extent to which these heavy hydrocarbon constituents are less well-defined and understood than light ones is partly a reflection of the greater economic value enjoyed by the lighter ends and partly of the tractable experimental methods commonly used for light-end analysis. Standard laboratory methods such as gas chromatography can characterize components of the lighter, simpler hydrocarbon compounds with carbon numbers less than about 36. Even large alkanes are amenable to specialized chromatography. However, in the realm of the asphaltenes, standard methods are often not applicable, so extraordinary measures are required to extract accurate information about component structure.



^ Molecular structure of some saturates and aromatics. Saturates include methane, pentane and heptane. Benzene is the simplest aromatic.

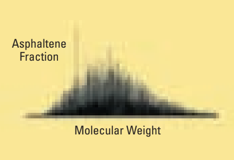
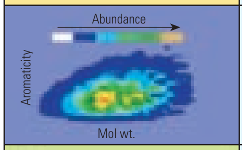
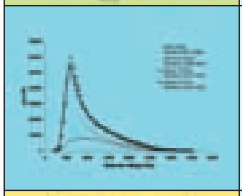
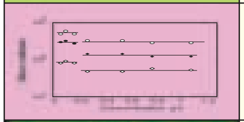
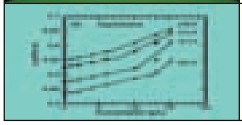
The list of techniques that have been used to study asphaltenes and other heavy fractions encompasses mass spectrometry, electron microscopy, nuclear magnetic resonance, small-angle neutron and X-ray scattering, ultrasonic spectroscopy, dynamic light scattering, fluorescence correlation spectroscopy, fluorescence depolarization, vapor-pressure osmometry and gel permeation chromatography. Because these methods investigate various aspects of asphaltenes under different conditions, it is not surprising that they have produced disparate models of asphaltene molecules.

Today, two main types of measurements—mass spectrometry and molecular diffusion—produce the most consistent evidence on asphaltene molecular weight and size (next page). Mass spectrometry induces a charge on the molecule, accelerates the resulting ion in an electromagnetic field, and measures the charge-to-mass ratio. Various types of mass spectrometry have different ways of ionizing molecules and accelerating ions.[4] A key resource for asphaltene studies using mass spectrometry is the National High Magnetic Field Laboratory at Florida State University in Tallahassee (see "Asphaltene Mass Spectrometry," *page 26*).

In molecular-diffusion measurements, various techniques, especially fluorescence techniques, track the diffusion of individual molecules.[5] Large molecules diffuse slowly, and smaller molecules diffuse more quickly. Estimates of molecular diameter are interpreted to infer molecular weight by comparison with model compounds.

In the 10 years since these techniques have become available, the concept of the asphaltene molecule has undergone a transformation. Because the asphaltene solubility classification captures a broad range of molecular structures, it is impossible to define a single molecular structure and size. However, a picture is emerging that honors results from several measurement types. This latest thinking puts the average molecular weight at about 750 g/mol within a range of 300 to 1,400 g/mol. That is

(continued on page 28)

Graphic icon	Method name	Brief description	Molecular weight or molecular size	Reference
	Field-ionization mass spectrometry (FI-MS)	Probe-vaporized asphaltenes passing through a high-energy electric field are ionized. Their mass-to-charge ratio is used to generate a mass spectrum.	800 g/mol	Boduszynski, reference 4
	Electrospray ionization, Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS)	This Nobel Prize-winning ionization method evaporates solvent from solute, allowing very large molecules to go into the vapor phase.	Most between 400 and 800 g/mol, with a range of 300 to 1,400 g/mol.	Rodgers and Marshall, reference 4
	Atmospheric pressure photoionization mass spectrometry (APPI MS)	Gas-nebulized samples are ionized by light to measure the mass-to-charge ratio of the asphaltenes.	750 g/mol, with a range of 400 to 1,200 g/mol	Merdrignac et al, reference 4
	Field-desorption/field-ionization mass spectrometry (FD-FI MS)	An asphaltene sample deposited on a needle-like surface is desorbed and ionized when heat and a high electric field are applied. The ion mass-to-charge ratio is used to generate the mass spectrum.	~ 1,000 g/mol with a broad distribution	Qian et al, reference 4
	Laser desorption ionization (LDI)	A laser pulse on a solid asphaltene sample creates a gas plume. Low laser power and low gas densities are required for accuracy.	800 to 1,000 g/mol	Hortal et al, reference 4
	Time-resolved fluorescence depolarization (TRFD)	Rotational diffusion constants of asphaltene molecules in solution are measured by detecting the rate of decay of induced polarization.	~ 2 nm diameter corresponding to 750 g/mol with a range between 500 and 1,000 g/mol	Groenzin and Mullins, reference 5
	Nuclear magnetic diffusion	Asphaltene molecules diffuse in an NMR field. Diffusion time is related to molecular size.	~ 2.6 nm diameter. Some dimers, or pairs of molecules, yield the larger size.	Freed et al, reference 5
	Fluorescence correlation spectroscopy (FCS)	Translational diffusion coefficients of fluorescing molecules lead to a length scale corresponding to a sphere-equivalent hydrodynamic radius.	~ 2.4 nm diameter corresponding to 750 g/mol. Smaller for coal asphaltenes.	Andrews et al, reference 5
	Taylor dispersion diffusion	The translational diffusion coefficient of molecules in laminar flow is related to molecular size.	~ 1.4 nm diameter for coal asphaltenes (same as Groenzin and Mullins, reference 5)	Wargadalam et al, reference 5

^ Some of the techniques that yield consistent results for asphaltene molecular weight and size. Descriptions of each technique are simplified summaries and are for illustrative purposes only. Mass spectrometry measurements (blue shading) give results in terms of molecular weight. Molecular diffusion measurements (yellow shading) give results in terms of molecular size, or diameter. Some other techniques, such as vapor-pressure osmometry and gel permeation chromatography, which are successful in characterizing lighter hydrocarbon compounds, give inconsistent values for asphaltene molecular weight.

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4. Boduszynski MW: "Asphaltenes in Petroleum Asphalts: Composition and Formation," in Bunger JW and Li NC (eds): *Chemistry of Asphaltenes*. Washington, DC: American Chemical Society (1981): 119–135.

   Rodgers RP and Marshall AG: "Petroleomics: Advanced Characterization of Petroleum-Derived Materials by Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)," in Mullins et al, reference 2: 63–94.

   Merdrignac I, Desmazières B, Terrier P, Delobel A and Laprévote O: "Analysis of Raw and Hydrotreated Asphaltenes Using Off-Line and On-Line SEC/MS Coupling," presented at the International Conference on Heavy Organics Deposition, Los Cabos, Baja California, Mexico, November 14–19, 2004.

   Qian K, Edwards KE, Siskin M, Olmstead WN, Mennito AS, Dechert GJ and Hoosain NE: "Desorption and Ionization of Heavy Petroleum Molecules and Measurement of Molecular Weight Distributions," *Energy & Fuels* 21, no. 2 (March 2007): 1042–1047.

   Hortal AR, Martínez-Haya B, Lobato MD, Pedrosa JM and Lago S: "On the Determination of Molecular Weight Distributions of Asphaltenes and Their Aggregates in Laser Desorption Ionization Experiments," *Journal of Mass Spectrometry* 41, no. 7 (July 2006): 960–968.

5. Groenzin H and Mullins OC: "Molecular Size and Structure of Asphaltenes from Various Sources," *Energy & Fuels* 14, no. 3 (May 2000): 677–684.

   Freed DM, Lisitza NV, Sen PN and Song Y-Q: "Molecular Composition and Dynamics of Oils from Diffusion Measurements," in Mullins et al, reference 2: 279–300.

   Andrews AB, Guerra RE, Mullins OC and Sen PN: "Diffusivity of Asphaltene Molecules by Fluorescence Correlation Spectroscopy," *Journal of Physical Chemistry* A 110, no. 26 (July 6, 2006): 8093–8097.

   Wargadalam VJ, Norinaga K and Iino M: "Size and Shape of a Coal Asphaltene Studied by Viscosity and Diffusion Coefficient Measurements," *Fuel* 81, no. 11–12 (July 2002): 1403–1407.

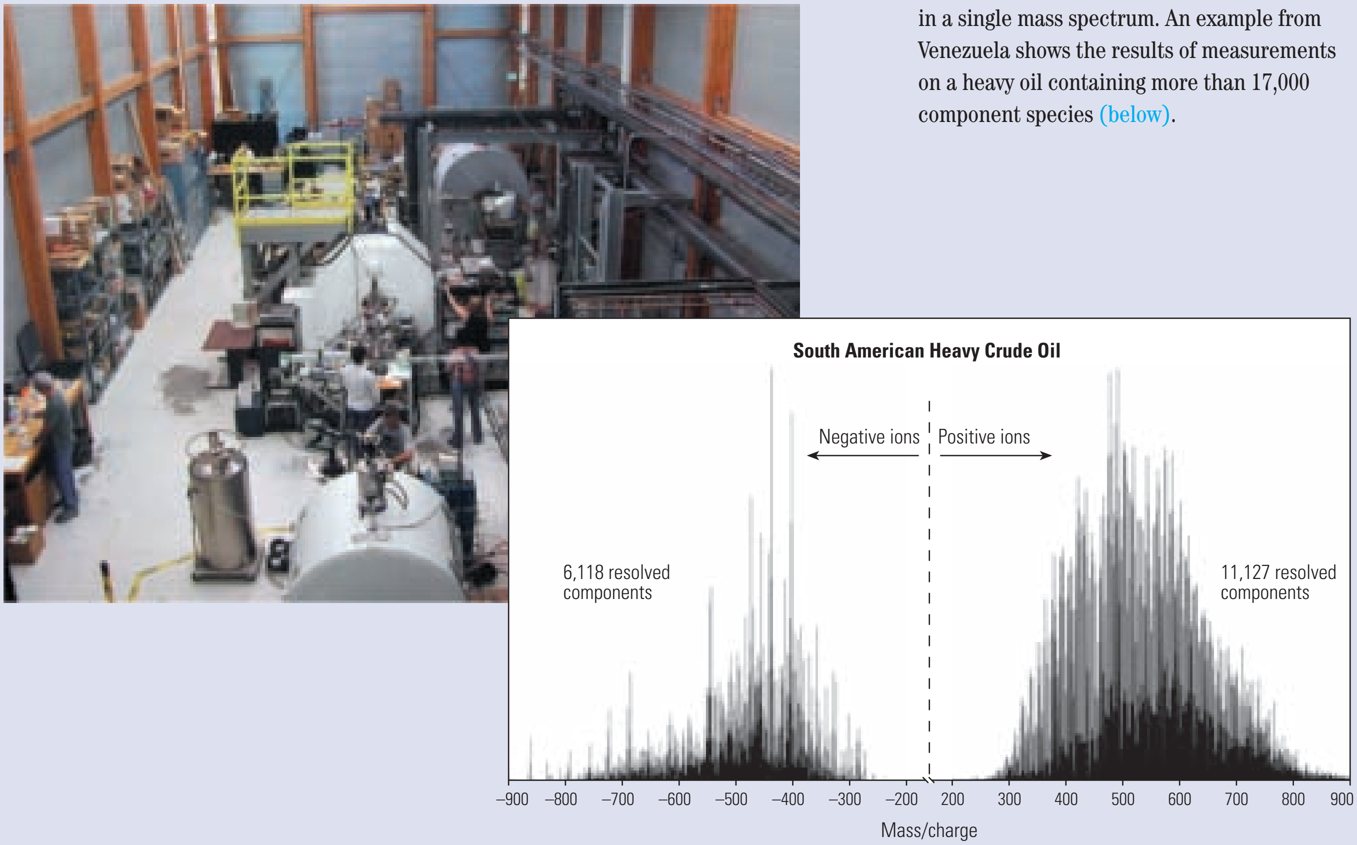
Asphaltene Mass Spectrometry

Remarkably, the mass corresponding to any one molecular elemental composition, for example, $C_cH_hN_nO_oS_s$, is unique. This uniqueness holds for molecules up to 1,000 dalton (Da) in mass, and provided that the molecular mass can be measured to within about 100 parts per billion (ppb), or 0.001 of the mass of a hydrogen atom.[1] For example, two molecules that differ in composition by C_3 versus SH_4, both weighing 36 Da, differ in mass by 0.0034 Da—less than seven times the mass of an electron! However, this difference can be resolved by mass spectrometry.

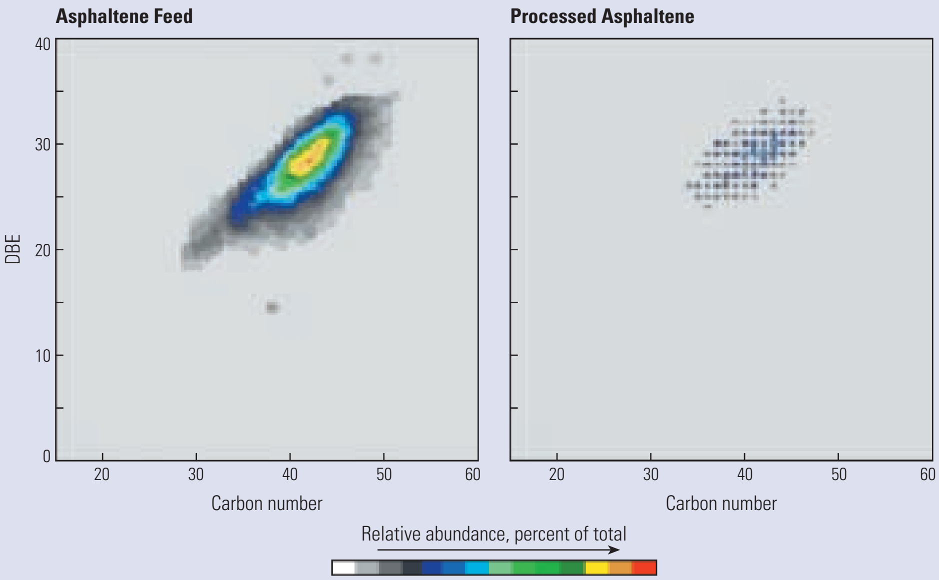
Mass spectrometry can resolve and identify molecules based on mass, provided that the molecule can be ionized, that is, charged, and vaporized. The electrospray ionization technique, for which John Fenn won the 2002 Nobel Prize, can either remove a proton from a neutral acidic molecule, M, to form an $(M\text{-}H)^-$ ion or add a proton to a neutral basic molecule to yield an $(M+H)^+$ ion. Electrospray ionization can thus be used to access the polar molecules in petroleum, such as asphaltenes.

The mass of the ions can be resolved with ultrahigh accuracy by placing them in a magnetic field. In a magnetic field, the ion cyclotron rotational frequency is inversely proportional to ion mass, and can be measured to the required 100-ppb precision by Fourier transform (FT) ion cyclotron resonance (ICR) mass spectrometry (MS). Introduced in 1974, FT-ICR MS offers 10 to 100 times higher mass resolution and mass accuracy than other mass analyzers, and is the only mass-analysis method capable of resolving the chemical constituents of petroleum.[2]

The FT-ICR mass spectrometers at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Florida, can resolve up to 20,000 different elemental compositions in a single mass spectrum. An example from Venezuela shows the results of measurements on a heavy oil containing more than 17,000 component species (below).



^ Facilities and measurements at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Florida. Instrumentation at the laboratory (*left*) consists of three large magnets, which are contained in horizontally oriented cylindrical housings and operate at magnetic-field intensities of 9.4 teslas, 9.4 teslas and 14.5 teslas (from foreground to background). An example mass-spectrometry output (*right*) shows the number of negatively and positively charged components that can be resolved from a South American heavy-oil sample.



^ Multidimensional characterization of a crude oil. Once the elemental compositions of the components of a crude oil have been identified by mass spectrometry, the components are sorted by heteroatom class. This example shows the characterization of those species containing one sulfur atom. Plotted on the vertical axis is the double-bond equivalent (DBE), which is related to the number of carbon and hydrogen atoms in a molecule. The plot on the left depicts the characterization of these sulfur-bearing molecules in the crude oil, and the plot on the right displays the characterization after the oil has undergone hydrodesulfurization.

Once the species have been identified, the next step is to sort them by heteroatom class, or numbers of N, O and S atoms. Moreover, every additional ring or double bond requires the loss of two hydrogen atoms. Thus, knowledge of the numbers of C and H atoms in a molecule determines its number of rings plus double bonds; this sum is known as the “double-bond equivalent,” or DBE, defining the molecular “type.” Once the DBE is known, the remaining carbons must be aliphatic, for example, bound as CH_2 or CH_3.[3]

It thus becomes possible to characterize a crude oil by mapping its characteristics in multiple dimensions, such as heteroatom relative abundance, DBE and carbon number. As an example of this technique applied to crude-oil processing, the relative abundance of species containing one sulfur atom can be plotted before and after hydrodesulfurization (above). These plots can be used to assess the effectiveness of processing methods.

These high-resolution measurements facilitate new understanding of petroleum constituents. The new field of “petroleomics” is based on the premise that sufficiently complete knowledge of the chemical composition of petroleum should enable correlation, and ultimately prediction, of its properties and behavior. The NHMFL group is laying the groundwork for such correlations to characterize deposits, heavy ends and asphaltenes, changes introduced by distillation and hydrotreatment, corrosion and oil-water emulsions.[4] For example, the group has confirmed and extended prior independent optical measurements by Schlumberger researchers to show that even the heavy-end petroleum fraction is composed primarily of molecules less than 1,000 Da in molecular weight.[5] The method also enables interfacially active components to be determined so that wettability and its effects can be understood. Ongoing and future applications are aimed at the analysis of downhole fluids to detect compartmentalization and identify potential production problems.

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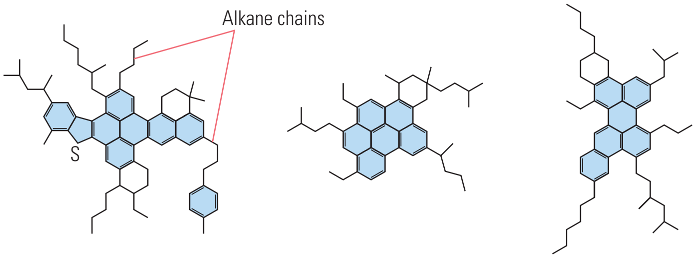
1. One dalton equals one atomic mass unit, and is defined as one-twelfth of the mass of an unbound atom of carbon-12.
2. Comisarow MB and Marshall AG: “Fourier Transform Ion Cyclotron Resonance Spectroscopy,” *Chemical Physics Letters* 25 (1974): 282–283.
   Marshall AG, Hendrickson CL and Jackson GS: “Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: A Primer,” *Mass Spectrometry Reviews* 17 (1998): 1–35.
3. Aliphatic compounds are organic compounds in which carbon atoms are joined in chains or rings, with no double bonds. Examples are n-pentane, n-hexane and benzene.
4. Marshall AG and Rodgers RP: “Petroleomics: The Next Grand Challenge for Chemical Analysis,” *Accounts of Chemical Research* 37, no. 1 (2004): 53–59.
   Rodgers RP, Schaub TM and Marshall AG: “Petroleomics: Mass Spectrometry Returns to Its Roots,” *Analytical Chemistry* 77 (2005): 20A–27A.
5. Mullins et al, reference 2, main text.

compatible with a molecule containing seven or eight fused aromatic rings, and the range accommodates molecules with four to ten rings (below). There is also evidence that some asphaltenes consist of multiple groups of rings linked by alkane chains.[6]

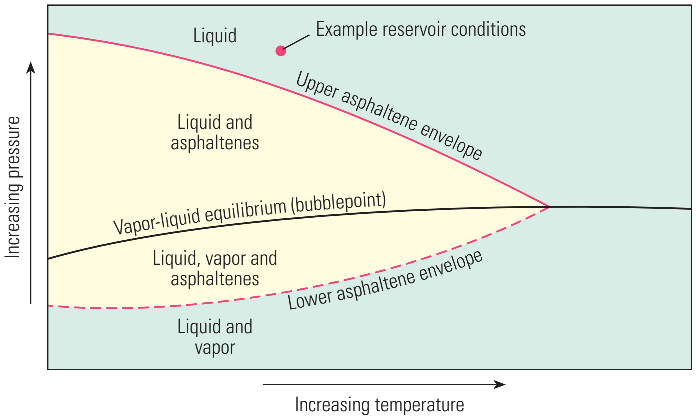
Heteroatoms, which are largely contained in the ring systems, can give the molecule polarity: the polarizability of the fused aromatic-ring systems and the charge separation induced by heteroatoms cause the centers of neighboring asphaltene molecules to stick to each other, while the outer chains are repulsed by the chains of other molecules. Such a structure is consistent with the Yen model suggested more than 40 years ago, which also proposed stacking asphaltene fused-ring systems.[7] However, the molecular weight of a single molecule is significantly smaller—by a factor of ten—than the average asphaltene molecular weight proposed in the 1980s and 1990s. Only now is the Yen model understood within a framework of asphaltene molecular structure and aggregation.



Asphaltene Molecules

^ Asphaltene molecular structures. Shown here are three of the many possible structures of asphaltenes, which are a class of molecules composed of grouped aromatic rings (blue) with alkane chains. Some rings may be nonaromatic. Many of the rings are fused, meaning the rings share at least one side. Heteroatoms such as sulfur, nitrogen, oxygen, vanadium and nickel may reside in the aromatic rings. The molecule on the left contains a heteroatom in the form of sulfur [S]. Some asphaltenes consist of multiple groups of rings linked by alkane chains. The molecule on the left contains two such groups—one with ten rings and one with a single ring.

Asphaltene-Precipitation Envelope



^ The asphaltene-precipitation envelope (APE) in pressure-temperature space. The asphaltene-precipitation envelope (red curve) delimits the stability zones for asphaltenes in solution. For given example reservoir conditions (red dot), primary depletion causes pressure to decrease. When pressure reaches the upper asphaltene-precipitation envelope, also known as the asphaltene-precipitation onset pressure, the least-soluble asphaltenes will precipitate. As pressure continues to decrease, more asphaltenes will precipitate, until the bubblepoint pressure is reached, and gas is released from solution. With continued pressure decrease, enough gas has been removed from the system, and the crude oil may begin to redissolve asphaltenes at the lower asphaltene-precipitation envelope. (Modified from Jamaluddin et al, reference 16.)

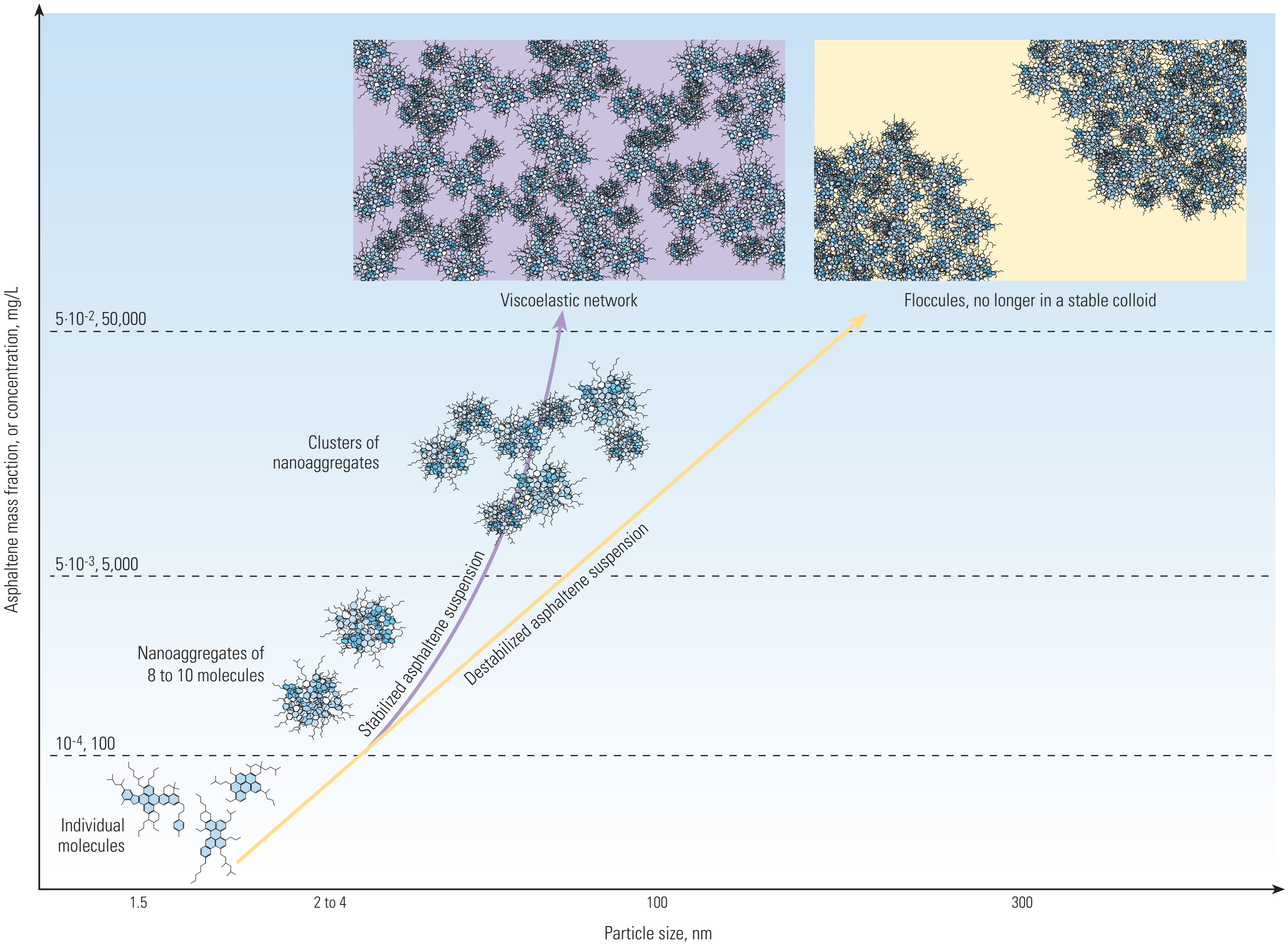
Using the size and structure of an individual molecule as a starting point, chemists can now explain how asphaltene molecules behave before they precipitate (next page). This aggregation behavior depends on solvent type. Most laboratory studies are conducted with asphaltenes dissolved in a solvent, such as toluene, but some are performed with asphaltenes in their native crude oil.

At extremely low concentrations, below 10^{-4} mass fraction, asphaltene molecules in toluene are dispersed as a true solution.[8] At higher concentrations in toluene, on the order of 10^{-4} mass fraction, asphaltene molecules stick together to form nanoaggregates, or nanometer-sized particles. These nanoaggregates are dispersed in the fluid as a nanocolloid, meaning the nanometer-sized asphaltene solids are stably suspended in the continuous liquid phase. The concentration at which nanoaggregates form was first revealed by ultrasonic methods, but has been confirmed more recently by nuclear magnetic resonance diffusion measurements and conductivity results.[9] As concentration reaches approximately 5 g/L, or mass fraction of $5\cdot10^{-3}$, the nanoaggregates appear to form clusters.[10] The clusters remain in stable colloidal suspension until asphaltene concentration reaches a mass fraction of roughly 10^{-2}. At higher concentrations in toluene, the asphaltene clusters flocculate, forming clumps, which are no longer stable in toluene, and so they precipitate.

In crude oil, the picture is even less clear, for several reasons. Most experimental methods become difficult to interpret in crude oils. Also, the presence of other compounds in crude oil affects asphaltene solubility. A recent study points to evidence of asphaltenes as nanoaggregates in crude-oil samples analyzed downhole.[11] Laboratory experiments, discussed in the next section, show how changes in pressure, temperature or composition can cause asphaltenes in crude oil to flocculate and form thick deposits. However, in some crude oils, asphaltenes can remain in a stable "solution" at extremely high concentration without precipitating. For example, Athabasca bitumen can contain more than 18% asphaltene in a stable viscoelastic network.[12] Experts agree that more work is required to characterize asphaltene behavior in crude oils.

Laboratory Precipitation Methods: Asphaltenes in Crude Oil

Crude oils that exhibit asphaltene precipitation and deposition during primary depletion are typically undersaturated, meaning they exist in



^ A way of looking at aggregation behavior of asphaltenes with increasing concentration. Asphaltenes exhibit different aggregation properties depending on whether they are dissolved in crude oil (purple) or toluene (yellow). Individual molecules are seen only at low concentrations, below 100 mg/L, or 10^{-4} mass fraction. As concentration increases, molecules stick together, first in pairs, then in greater numbers. Once concentration rises to about 100 mg/L, or 10^{-4} mass fraction, the molecules form near-spherical nanoaggregates of eight to ten molecules stacked together. At higher concentration levels, greater than 5,000 mg/L, or mass fraction of $5\cdot10^{-3}$, nanoaggregates form clusters, in which the bodies of the nanoaggregates do not overlap, but the alkane chains of neighboring clusters may interact. These clusters may remain in stable colloidal suspension until concentration reaches a mass fraction of 10^{-2}. Stability can continue to even higher concentrations in crude oil, where clusters may form a viscoelastic network. However, in toluene, high concentrations cause the asphaltene clusters to flocculate.

the reservoir at pressures higher than the bubblepoint pressure. These crude oils tend to have low asphaltene content and high gas content. During reservoir production at a constant temperature, once pressure decreases to intersect the asphaltene-precipitation envelope (APE), also known as the asphaltene-precipitation onset pressure, dissolved asphaltenes start to precipitate and potentially deposit in the reservoir and flowlines (previous page, bottom). Typically, the amount of precipitated asphaltene increases as the pressure decreases, and reaches a maximum at the bubblepoint pressure. The pressure-temperature (P-T) line

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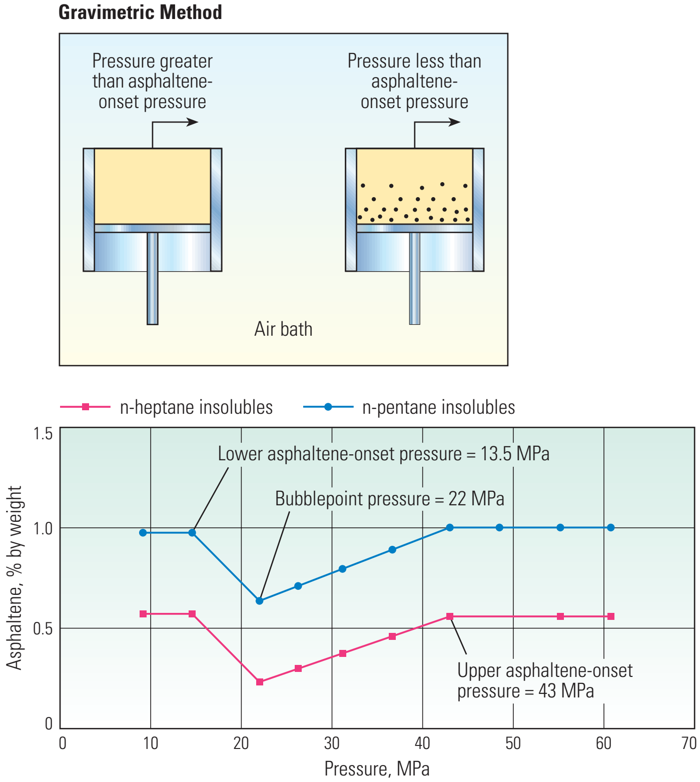


^ Gravimetric detection of asphaltene precipitation in a Middle East oil. SARA fractionation determined asphaltene content of the fluid remaining after precipitating asphaltenes using n-pentane (blue circles) and n-heptane (red squares). Both types of asphaltenes showed the same precipitation tendencies. The precipitation-onset pressure determined gravimetrically was 42.75 MPa [6,200 psi] for both types. Asphaltene content in the remaining liquid continued to decrease until pressure reached 22.24 MPa [3,225 psi], corresponding to the bubblepoint pressure. Additional pressure reduction caused dissolved asphaltene concentration to rise until pressure reached the lower asphaltene boundary at 13.5 MPa [1,960 psi], after which the asphaltene content stabilized at its original level. (Modified from Jamaluddin et al, reference 16.)

delineating the precipitation conditions above the bubblepoint is called the upper boundary of the asphaltene-precipitation envelope.

As pressure continues to decrease below the bubblepoint pressure, solution gas is removed from the oil, causing the oil to become denser and more optically refractive. Depressurization below the bubblepoint may lead to redissolution of the previously precipitated asphaltenes if the system is vigorously mixed and if asphaltene redissolution kinetics are relatively fast.[13] In this case, the P-T diagram features a lower boundary of the asphaltene-precipitation envelope, below which the asphaltenes redissolve into solution. However, because pressure-induced asphaltene redissolution kinetics can be slow, the lower boundary of the asphaltene-precipitation envelope can be difficult to identify experimentally.[14]

Identifying the conditions at which asphaltenes precipitate is the first step in seeking a solution to a potential asphaltene problem. To identify these conditions, two types of laboratory experimental programs are conducted in advance of any field development plan. Initially, precipitation measurements are performed to determine asphaltene-precipitation onset pressures at constant temperature or onset temperatures at constant pressure.[15] Since the precipitation of asphaltene does not necessarily lead to asphaltene sticking or deposition, it is important to also conduct deposition measurements at realistic production conditions of temperature, pressure, composition and shear. The deposition tests help to assess the deposition tendency of pressure-induced asphaltenes and to estimate the rate of deposition.

Various laboratory techniques have been developed for studying asphaltene precipitation from live crude oil.[16] Methods such as gravimetric precipitation, acoustic resonance and filtration have been used to determine asphaltene-onset pressure. Other techniques, such as light scattering, high-pressure microscopy and particle-size analysis, have gained wide acceptance within the flow-assurance community, and have become industry standards for screening reservoir fluids for asphaltene, wax and hydrate stability. Each technique measures a different property of the fluid as pressure decreases. Combining results from several methods increases confidence in the quantification of the APE.

In the gravimetric method, asphaltenes precipitate and fall to the bottom of a pressure-volume-temperature (PVT) cell. At selected pressure steps, samples of the remaining fluid are analyzed through SARA fractionation, and show a decrease in concentration of asphaltenes. The method provides data for an asphaltene concentration-versus-pressure plot, with transitions that correspond to the upper and lower boundaries of the asphaltene-precipitation envelope. The accuracy of this method is limited by the selection of pressure steps and the accuracy of the asphaltene-concentration measurements. Greater accuracy requires small intervals between pressure measurements, so the experiment may be time-consuming and requires large volumes of reservoir fluid. Also, this method may be subjective in estimating the onset of asphaltene precipitation because the onset point may be missed if the pressure steps are too large.

In one example, the gravimetric method detected asphaltene precipitation in an oil from the Middle East.[17] Asphaltenes insoluble in n-pentane and asphaltenes insoluble in n-heptane were precipitated by SARA fractionation remaining after the gravimetric method (above left). Measurements were performed at the reservoir temperature of 116°C [240°F].

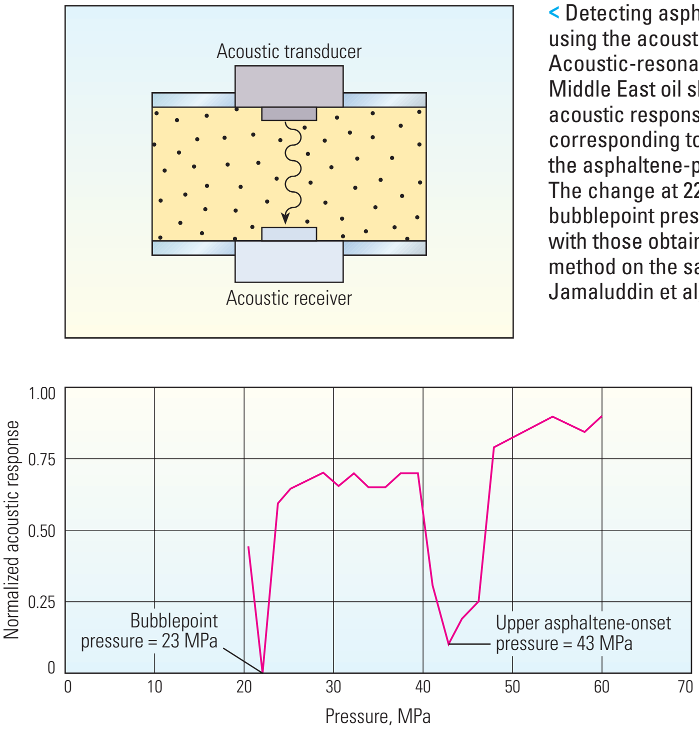
Another method, the acoustic-resonance technique (ART), measures changes in the acoustic properties of the fluid as asphaltenes drop out of solution. The additional solids in the mixture increase the stiffness of the system. As pressure decreases, an acoustic receiver on one end of a PVT cell detects acoustic resonance generated by an acoustic transducer at the other end of the cell. The acoustic system is accurate to ± 100 psi [0.69 MPa] and requires only 10 mL of single-phase reservoir fluid. The ART is less time-consuming than the gravimetric method. As for disadvantages, the resonance changes detected by the ART are not unique to asphaltene precipitation; the presence of other solids and vapor-liquid phase boundaries could cause similar changes in acoustic properties. Also, the technique does not allow the fluid to be mixed, giving rise to potentially inaccurate onset measurements caused by heterogeneous distribution of asphaltenes. Furthermore, the method does not detect the lower boundary of the asphaltene-precipitation envelope. This may be because the dissolution of asphaltene is a gradual phase transition.

The acoustic-resonance technique was used to examine asphaltene precipitation in the same Middle East oil (right). As with the gravimetric method, measurements were taken at the reservoir temperature of 116°C. The asphaltene-onset pressure obtained by the ART agrees with the results obtained by the gravimetric method.

The light-scattering technique (LST), also known as the DBR solids-detection system (SDS), uses near-infrared light to probe fluids as asphaltenes precipitate either isothermally with decreasing pressure or isobarically with decreasing temperature. In the Oilphase-DBR fluid sampling and analysis laboratory setup, the PVT cell used for this technique is a transparent glass tube containing a magnetically driven mixer.[18] A near-infrared (NIR) light source on one side of the cell generates light at wavelengths between 800 and 2,200 nm at a specific transmittance power. When asphaltenes precipitate, they scatter light, reducing the transmittance power of the light detected by fiber-optic sensors on the other side of the cell. As with the acoustic-resonance technique, the advantages of the light-scattering method are speed of testing and the low volume of single-phase reservoir fluid required.

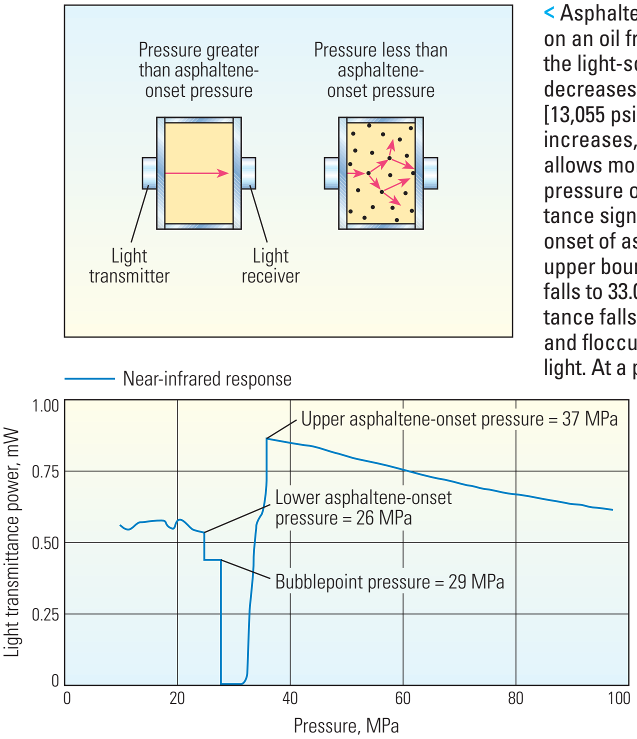
Results of the light-scattering technique applied to isothermal depressurization of an oil from the Gulf of Mexico show a typical response (right). The drop in the power of transmitted light at 36.54 MPa [5,300 psi] marks the upper

Acoustic-Resonance Technique



< Detecting asphaltene precipitation using the acoustic-resonance technique. Acoustic-resonance measurements on a Middle East oil show a sharp change in acoustic response at 42.92 MPa [6,225 psi], corresponding to the upper boundary of the asphaltene-precipitation envelope. The change at 22.68 MPa [3,290 psi] is the bubblepoint pressure. These results agree with those obtained using the gravimetric method on the same oil. (Modified from Jamaluddin et al, reference 16.)

Near-Infrared Light Scattering



< Asphaltene-precipitation measurements on an oil from the Gulf of Mexico, using the light-scattering technique. As pressure decreases from a high of more than 90 MPa [13,055 psi], the light transmission power increases, because the less dense fluid allows more transmission of light. At a pressure of 36.54 MPa, the light transmittance signal (blue) plunges, signaling onset of asphaltene precipitation and the upper boundary of the APE. When pressure falls to 33.09 MPa [4,800 psi], the transmittance falls even farther, as large clusters and floccules of asphaltene scatter all light. At a pressure of 29.37 MPa [4,260 psi], light transmittance increases as bubbles of gas are created at the bubblepoint. This response is in contrast to that of some oils, which exhibit decreased transmittance with the appearance of bubbles. With continued depressurization, light transmittance jumps at 26 MPa, when asphaltenes start to redissolve. This is the lower boundary of the APE. (Modified from Jamaluddin et al, reference 16.)

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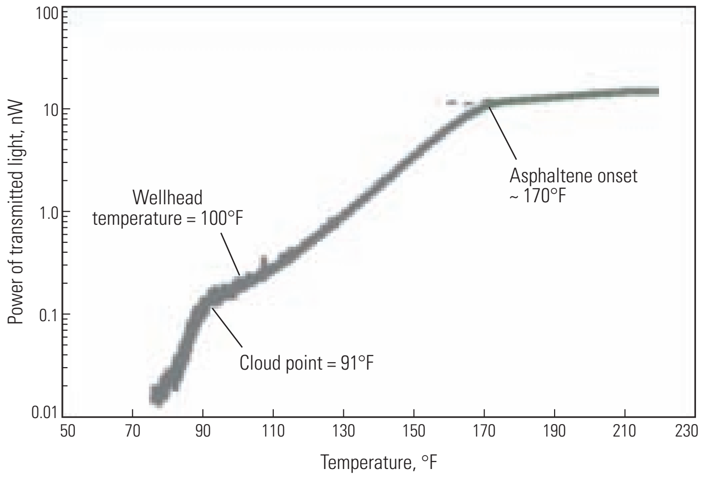
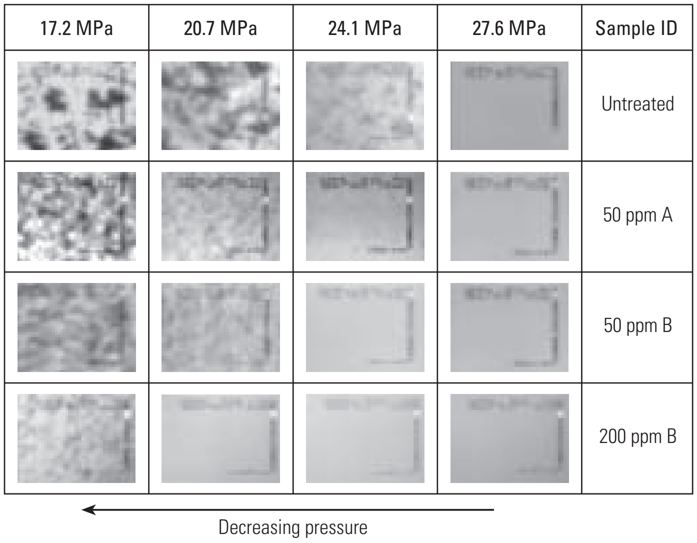


^ Light-scattering assessment of asphaltene onset during an isobaric temperature decrease. In this South American crude oil, asphaltenes began precipitating when the temperature reached 170°F [76°C]. Measurements were conducted at 4,000 psi [27.6 MPa]. Also shown is the cloud point—the temperature at which wax solidifies. (Modified from Hammami and Ratulowski, reference 14.)



^ High-pressure microscope (HPM) photographs of treated and untreated South American crude oil as pressure decreases. In the untreated oil (top row), dark particles interpreted as precipitated asphaltenes appear at a pressure of 24.1 MPa [3,500 psi], and they grow larger as pressure continues to decrease. After treatment with 50 ppm of asphaltene-precipitation inhibitor A (second row), some particulate matter can be detected again at 24.1 MPa. However, the particles are smaller, and remain smaller than those in the untreated oil as pressure decreases. This indicates that the inhibitor had some effect on asphaltene stability. When the oil is treated with 50 ppm of inhibitor B (third row), asphaltene particles appear at a lower pressure than in the previous cases, and so chemical B is a more effective precipitation inhibitor. Treatment with 200 ppm of inhibitor B (bottom row) depresses the asphaltene-precipitation onset pressure even further. (Modified from Karan et al, reference 19.)

APE, and the rise at 26 MPa [3,770 psi] points to the lower APE. In another case, the method was used with isobaric temperature decrease to detect asphaltene precipitation in a South American crude (left).

For comparison, the Gulf of Mexico oil was studied through filtration experiments in an Oilphase-DBR laboratory. In filtration measurements, the same PVT cell used in the light-scattering test is charged with 60 mL of single-phase reservoir fluid. A magnetic mixer agitates the cell contents as they are depressurized at reservoir temperature. At selected pressures, a small amount of fluid is extracted from the cell and passed through a 0.45-µm filter while maintaining pressure and temperature. SARA analysis of the compounds trapped by the filter tracks the change in asphaltene content as pressure decreases.

An advantage of the filtration technique is that it quantifies the amount of precipitated asphaltene. The technique can be used to define the upper and lower asphaltene phase boundaries. Another advantage of the filtration technique is that the asphaltenes are physically extracted from the oil, and so may be further characterized through mass spectrometry, molecular-diffusion studies or SARA analysis. However, unlike other methods, results depend on filter size. The filtration technique also requires more time than measuring acoustic resonance or light scattering.

Another advance, the DBR high-pressure microscope (HPM), allows direct visual observation of multiple phases present at elevated pressure and temperature. This technique allows microscopic visualization of the appearance of asphaltene particles as pressure decreases.[19] In one example, high-pressure micrographs helped assess the effectiveness of different precipitation inhibitors on a crude oil from South America (left). The micrographs show an increase in the size of asphaltene particles in the untreated oil as pressure decreases. The addition of chemical inhibitor A changes the aggregation characteristics of the asphaltenes: asphaltene particles become apparent at the same onset pressure as for the untreated oil, but the particles are much smaller, and remain smaller even as pressure continues to decrease. Inhibitor B is more effective at preventing asphaltene precipitation than inhibitor A.

The HPM images can also be used to validate results obtained from the light-scattering technique. A break in the light-transmittance curve signifies a change in the fluid. HPM micrographs taken at selected pressures help confirm the onset point determined by the LST (right).

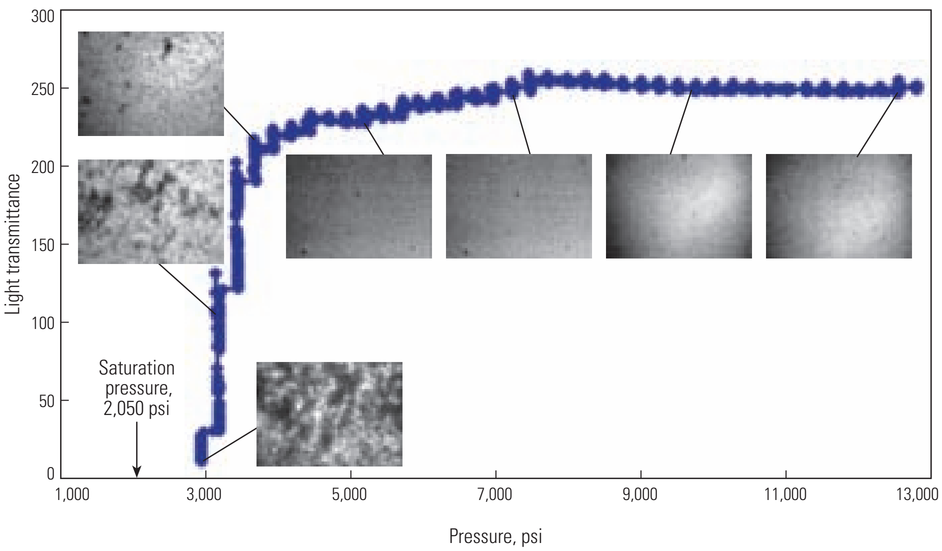
Although HPM is a direct and useful technique, it provides only a qualitative indication of particle size and number. To quantify these parameters, DBR scientists have developed proprietary particle-size analysis (PSA) imaging software to analyze HPM photographs. The PSA software scans digital HPM images as they are acquired and delivers quantitative information on relative abundance and size of particles, morphology changes and onset conditions.

Particle-size analysis on another crude oil from South America demonstrates the output of the image-analysis software (below right). Light-scattering measurements on this untreated oil had determined the asphaltene-precipitation onset pressure to be 5,500 psi [37.9 MPa]. The PSA results indicated a jump in particle size and particle count as pressure decreased to the precipitation-onset value. The size and number continued to increase as pressure dropped even further.

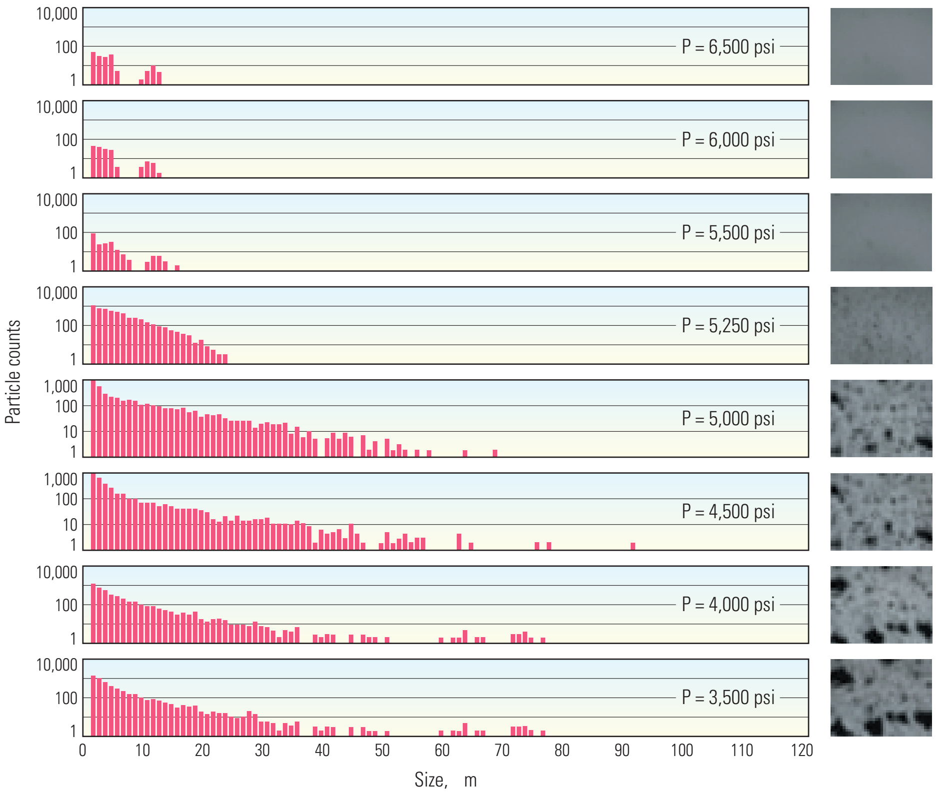
Laboratory Measurements of Asphaltene Deposition

Although asphaltene precipitation is a necessary condition for the formation of obstructions, it is not a sufficient condition. After precipitation, asphaltene particles must deposit and stick to a surface before they can become a flow-assurance problem.

While asphaltene precipitation is mainly a function of temperature, pressure, fluid composition and particle concentration, asphaltene deposition is a much more complex process and depends in addition on flow shear rate, surface type and characteristics, particle size and particle-surface interactions.



^ Light-transmittance trace acquired during isothermal depressurization of a South American crude oil. High-pressure micrographs taken at selected pressures yield direct evidence of asphaltene precipitation. The asphaltene-onset pressure is 7,500 psi [51.7 MPa] at reservoir temperature, corresponding to the initial gentle drop in the power of transmitted light and the first observed asphaltene particles. Below about 4,000 psi, the precipitated asphaltene particles start to agglomerate, leading to the dramatic drop in the power of transmitted light.



^ Particle-size analysis (PSA) generated during discrete depressurization of a South American crude oil. HPM images (*right*) were taken at pressures above, equal to and below the asphaltene-precipitation onset pressure determined by independent measurements. The images were analyzed for the number and size of particles and plotted in histogram form (*left*). The number and size of particles increase strongly at 5,500 psi, which is the asphaltene-onset pressure. As pressure decreases, particle size and number increase. The small but finite particle count detected by PSA at the pressures above the onset pressure is attributed to the presence of impurities, such as water droplets, in the oil. The equivalent diameter is the diameter of a circle with an area equivalent to the area of the observed particle, and the count number is a cumulative value obtained from analysis of 20 images taken at the same pressure. (Modified from Karan et al, reference 19.)

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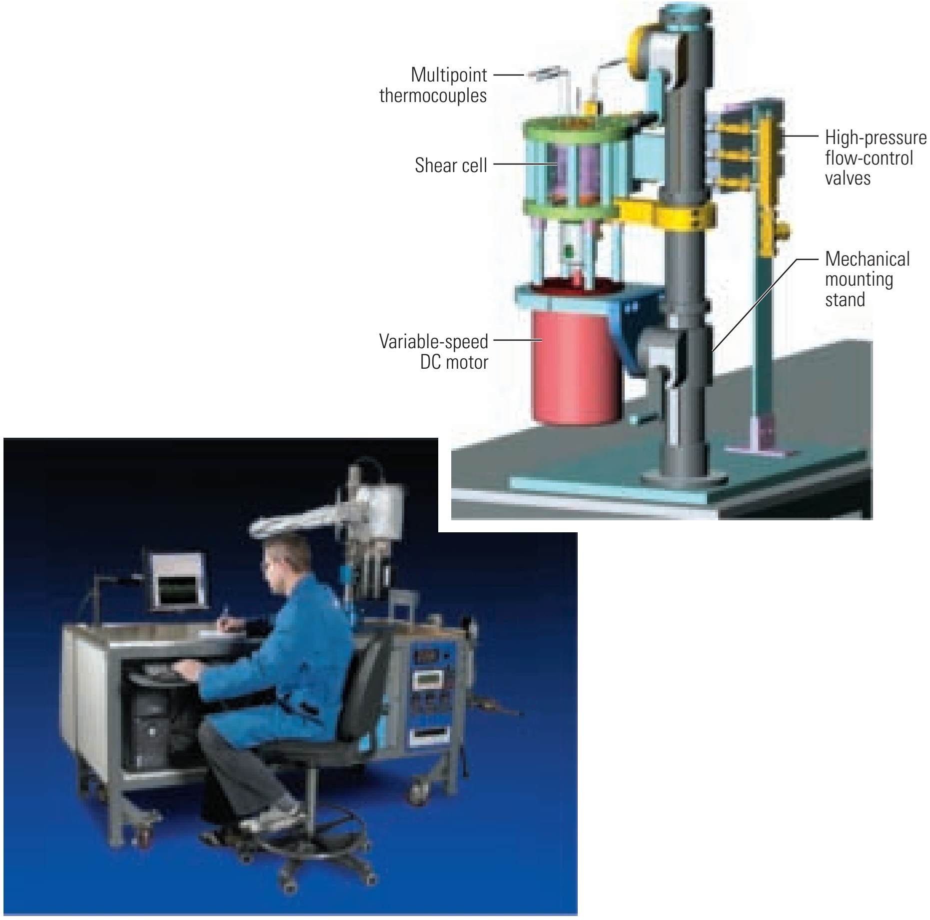


^ The organic solids deposition and control (OSDC) device. The apparatus simulates production flow under realistic conditions of pressure, temperature and composition for the study of asphaltene-deposition tendency. The OSDC tool helps optimize chemical treatment for the prevention and remediation of asphaltene deposition.

To investigate the tendency of organic solids to deposit under actual flow conditions, Oilphase-DBR scientists have built the organic solids deposition and control (OSDC) device (above).[20] The rotational movement of a spindle at the center of the device produces a fluid movement that creates a flow regime similar to pipe flow.

Unlike other deposition measurement techniques, the OSDC uses a relatively small volume—150 cm^3—of fluid and can operate at pressures up to 103.4 MPa [15,000 psi], temperatures up to 200°C [392°F] and Reynolds numbers up to 500,000.[21] The device can simulate production conditions of temperature, pressure, composition, surface type and either Reynolds number or wall shear stress. Through carefully designed and machined cylindrical inserts, the OSDC can also mimic surface roughness of tubulars. These key parameters can be accurately and independently controlled, allowing the deposition tests to be conducted over a wide range of conditions.

The OSDC device is often used to investigate the effect of chemical inhibitors on the deposition tendency of asphaltenes. Chemical treatment is one of the commonly adopted control options for the remediation and prevention of asphaltene deposition in production tubing. A typical inhibitor-selection test involves injecting a specified concentration of inhibitor into the reservoir fluid enclosed in the PVT cell and measuring the reduction of asphaltene-onset pressure of the inhibitor-treated oil as the fluid mixture depressurizes isothermally.

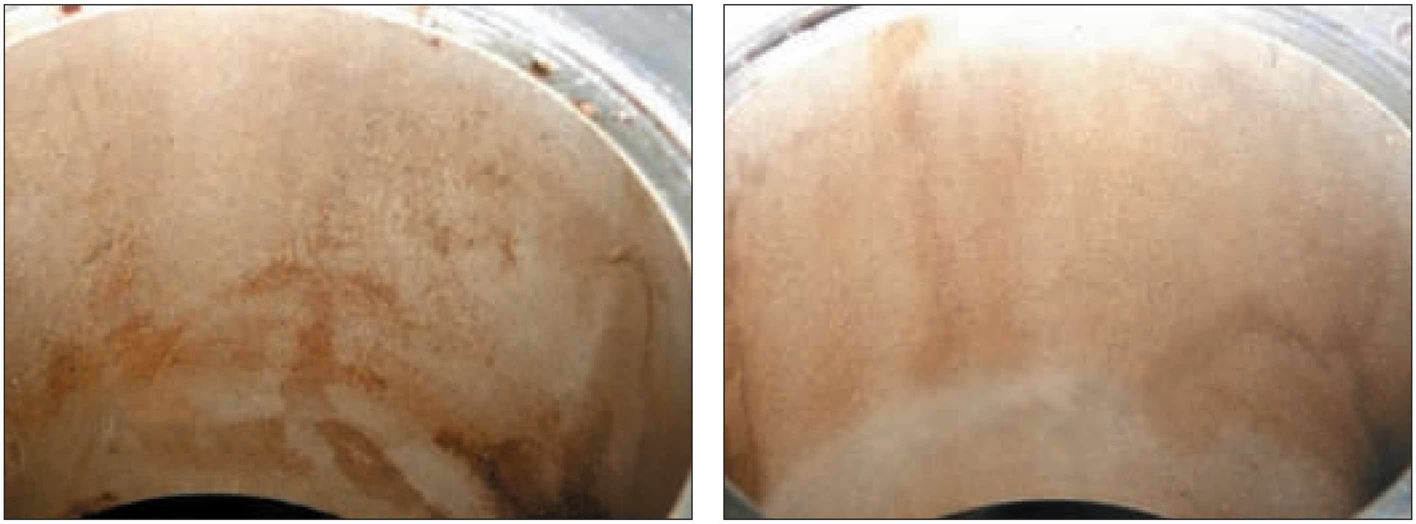
In one Gulf of Mexico example, a chemical inhibitor was tested for its effectiveness in preventing asphaltene deposition at reservoir temperature and at a pressure close to its saturation pressure. The initial screening performed by the chemical supplier on the stock tank oil sample had suggested that 200 ppm would inhibit the deposition of asphaltenes. OSDC tests on the treated and untreated oil indicated that asphaltenes would deposit on the OSDC wall whether the oil was chemically treated or not (next page, top). After completion of each test, the solids deposited on the wall were collected and analyzed to determine their asphaltene content using hot n-heptane. The analytical results showed that the suggested asphaltene inhibitor could not fully prevent asphaltenes from depositing on the wall, although it reduced the deposition rate of asphaltenes by approximately 40%.

The OSDC is the only commercially available device for studying the effects of asphaltene deposition in live oils and realistic flow regimes, allowing more accurate assessment of chemical-additive requirements. In one case, a customer used OSDC results to effect a fivefold reduction in chemical usage. By reducing the concentration of additive from 1,000 ppm to 200 ppm, annual chemical costs were cut by US $2.5 million.

A key factor in obtaining an accurate assessment of asphaltene precipitation and deposition in live oils is the quality of the fluid sample. For asphaltene studies, as for all fluid-analysis programs, it is vital that the sample be representative of reservoir fluid and be maintained at reservoir conditions throughout transport to the laboratory. Any sample-collection technique that fails to retain the single-phase nature of a sample risks significant errors in the subsequent analysis, especially for asphaltenes. Anecdotes abound of operators surprised by severe asphaltene problems because fluid samples had indicated no asphaltene content. Too late, they realized that fluid sample collection had taken place at pressure below bubblepoint, and asphaltenes that were in the fluid precipitated and adhered to the formation, leaving the sampled fluid free of asphaltenes.

Single-phase samples can be acquired using a variety of techniques at different times in the life of the field.[22] Common examples are the single-phase reservoir sampler (SRS) deployed during drillstem testing and the wireline-conveyed MDT Modular Formation Dynamics Tester run with a single-phase multisample chamber in open hole.[23] Representative samples can also be acquired with the CHDT Cased Hole Dynamics Tester in cased hole.[24]

A high-quality fluid sample is not only single-phase, but is also free of contamination. Contamination can cause large errors in laboratory measurements. For example, miscible oil-base mud (OBM) contamination in crude oil can change the measured asphaltene-precipitation onset pressure. Increasing the amount of contamination decreases the measured onset pressure. In one case, just 1% OBM contamination by weight caused asphaltene-precipitation



Untreated: 12 mg/h

Treated: 7 mg/h

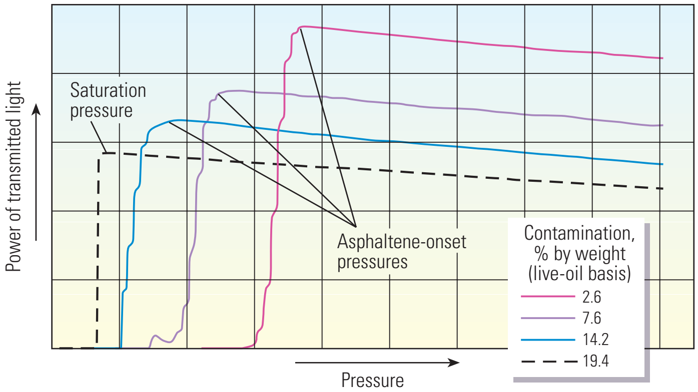
^ Assessing the effectiveness of an asphaltene-deposition inhibitor using OSDC tests. In one test, live oil from the Gulf of Mexico was left untreated (*left*), and subjected to reservoir flow conditions. In the second test, an asphaltene-deposition inhibitor chemical was mixed with the live oil (*right*) and the mixture was subjected to the same flow conditions. The OSDC results indicated both untreated and treated oils would deposit asphaltenes. However, the asphaltene-deposition inhibitor reduced the deposition rate of asphaltenes to 7 mg/h, compared with 12 mg/h in the untreated case.

onset pressure to decrease by 0.7 to 1.0 MPa [100 to 150 psi] (right).[25] These results underscore the need for low-contamination samples.

Modeling Asphaltene Behavior

Laboratory experiments to determine the asphaltene-precipitation envelope are usually conducted at reservoir conditions and also at a small selection of other temperatures and pressures. To better understand asphaltene behavior at the full range of conditions through which the fluid will pass on its way to the surface, models have been developed that attempt to honor experimental observations on asphaltene precipitation and deposition. These models can be divided into four groups: solubility models, solid models, colloidal models and association equation-of-state (EOS) models.

Solubility models—Solubility models are the ones most commonly applied to predict asphaltene precipitation. The first such model, established in 1984, employs a thermodynamic approach to describe asphaltene stability in terms of reversible solution equilibrium.[26] This version was easy to implement, but did not reproduce experimentally observed behavior. Since then, several researchers have crafted improvements, mainly on the calculation of asphaltene solubility parameters and the characterization of heavy fractions in crude oil. In the original version, a vapor-liquid equilibrium (VLE) was calculated to determine the



^ The effect of sample contamination on asphaltene-precipitation onset pressure. Measurements on hydrocarbon samples contaminated by oil-base drilling fluid can underestimate asphaltene-onset pressure. (Adapted from Muhammad et al, reference 25.)

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22. Aghar H, Carie M, Elshahawi H, Ricardo Gomez J, Saeedi J, Young C, Pinguet B, Swainson K, Takla E and Theuveny B: "The Expanding Scope of Well Testing," *Oilfield Review* 19, no. 1 (Spring 2007): 44–59.
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properties in liquid phase; then a liquid-liquid equilibrium (LLE) calculation—treating the asphaltene as a pseudoliquid—was performed, assuming no influence of the precipitated asphaltene phase on the previously calculated VLE. Later, researchers took the effect of asphaltene precipitation on the gas phase into account, and implemented a three-phase equilibrium calculation.[27] Work in 1995 extended the method to include polymer solution thermodynamics.[28] This more recent model can lead to a good representation of asphaltene behavior if calibrated by experimental results, but may not accurately estimate asphaltene precipitation in fluids with compositions different from those of the calibration crude oil.

Solid models—Solid models treat the precipitating asphaltene as a single, solid-phase component residing in a fluid whose phases are modeled using a cubic EOS. Solid models may require many empirical parameters and tuning to match experimental data. One solid model assumes the crude oil's heavy ends can be divided into precipitating and nonprecipitating components.[29] The precipitating components are taken to be asphaltenes. This model is easy to implement, but also requires experimental data to determine key parameters.

In another solid model, asphaltenes are treated as a lumped pseudocomponent, and all other components are considered solvent.[30] The method is simple, and allows direct calculation of asphaltene solubility, but does not include pressure effects, which are especially important to asphaltene stability.

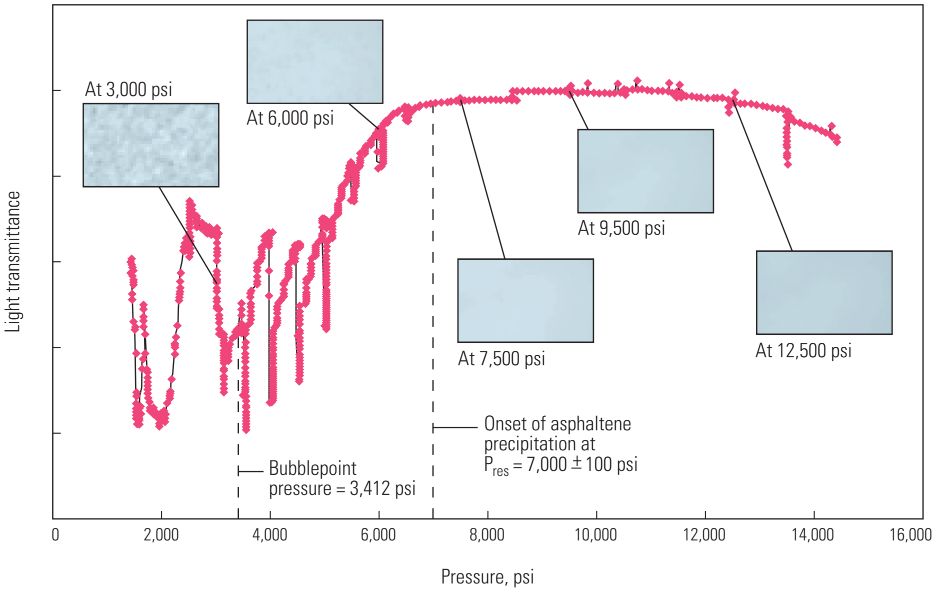
Colloidal models—Colloidal models have their basis in statistical thermodynamics and colloidal science. The first such model assumed asphaltenes exist in the oil as solid particles in colloidal suspension stabilized by resins adsorbed on their surfaces.[31] In this model, the vapor-liquid equilibrium calculated using an EOS establishes the composition of the liquid phase from which asphaltene may flocculate. Asphaltene-precipitation measurements at one set of conditions are interpreted to give a critical chemical potential for resins, which is subsequently used to predict asphaltene precipitation at other conditions.

Association equation-of-state (EOS) models—The asphaltene precipitation model developed by DBR, now a Schlumberger company, is an association EOS model.[32] This model makes four main assumptions:

- Asphaltene molecules exist mainly as monomers in the bulk crude oil and as aggregates in an associated state in the precipitation phase;
- Asphaltene association leads to asphaltene precipitation;
- The asphaltene precipitation process is thermodynamically reversible;
- The asphaltene-precipitation phase is a pseudoliquid phase.

This model combines terms describing the chemical and physical effects of association of asphaltene molecules. It requires composition, molecular weight, molecular size and interaction energy of each component.

To date, most of the above asphaltene-precipitation models have been tested only on limited sets of experimental results. Although most authors claim that their model could give reasonable predictions, none can be used to consistently predict asphaltene precipitation. However, these models all were developed before the emerging consensus on asphaltene molecular weight and structure. Until new models are developed that incorporate the most recent experimental findings, fluid chemists will continue to use the existing modeling methods.



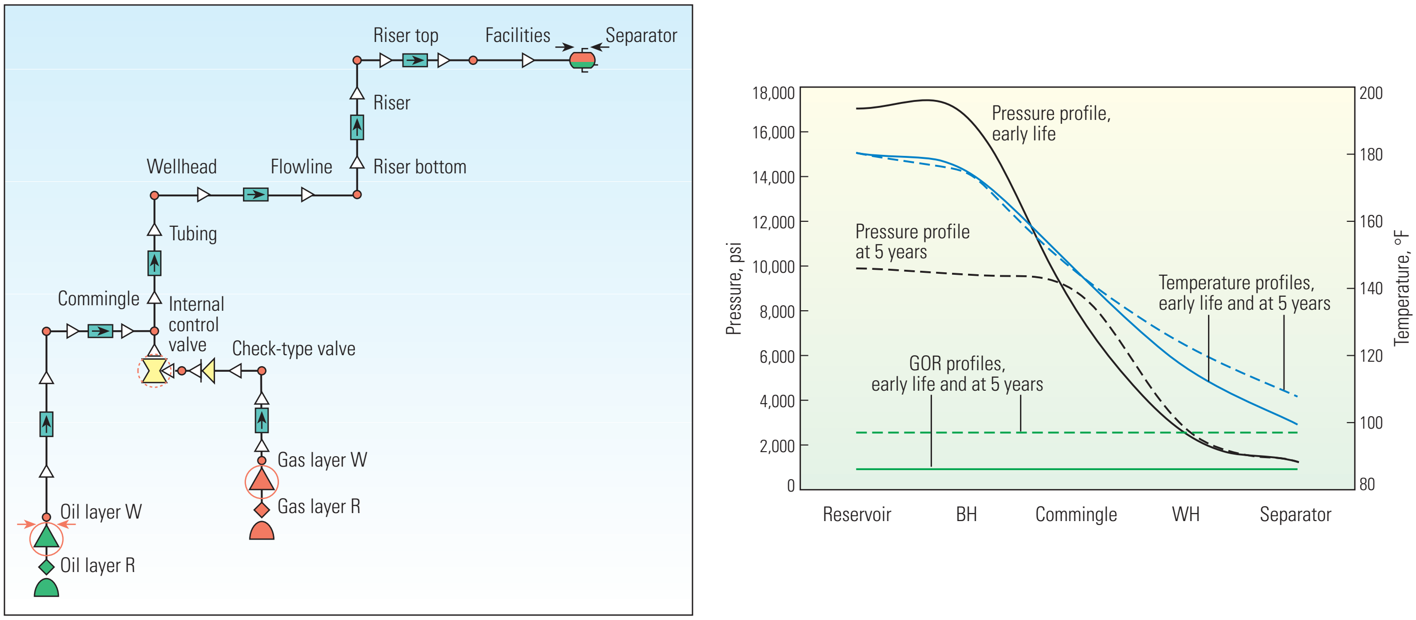
^ Near-infrared light-scattering measurements on a Gulf of Mexico oil from a Hydro well. Interpretation of the light-scattering readings (red dots) gave an asphaltene-onset pressure of 7,000 psi ± 100 psi. High-pressure microscopic photographs facilitated the visual interpretation of asphaltene-particle appearance and corroborated asphaltene onset at a pressure between 7,500 and 6,000 psi [51.7 and 41.4 MPa]. Bubbles were photographed at 3,000 psi, slightly below the bubblepoint pressure determined by PVT analysis. (Modified from Gonzalez et al, reference 33.)

Deepwater Gulf of Mexico Asphaltenes

Recently in the Gulf of Mexico, Hydro Gulf of Mexico LLC encountered potential asphaltene-precipitation problems in a deepwater development. Reserves in the two reservoir intervals were insufficient to justify constructing two production wells. A monobore subsea completion tapping both layers would need to be tied back to an existing platform for production to be economically viable. Because commingling of fluids results in a composition change that could cause asphaltenes to fall out of solution, the fluids and the entire production scenario had to be analyzed for potential asphaltene problems. Further compositional changes could be induced by injecting gas for gas lift, which was a completion method being considered. To reduce the risk of flow-assurance problems, scientists at Hydro, Schlumberger and Rice University in Houston adopted a systematic approach for early evaluation of the potential impact of asphaltene precipitation and deposition.[33]

Two wells penetrating the structure at different depths encountered two different fluids—oil and condensate. Laboratory measurements indicated that the two hydrocarbons were from different sources and were not in communication with each other. SARA fractionation of the oil revealed relatively low asphaltene content with 61.7% saturates, 26.0% aromatics, 11.4% resins and 0.9% asphaltenes.

Laboratory measurements with the near-infrared light-scattering technique gave the asphaltene-onset pressure as 7,000 psi [48.3 MPa] ±100 psi, and were corroborated by high-pressure microscopic photographs (left). However, the oil sample was known to contain 20% by weight OBM

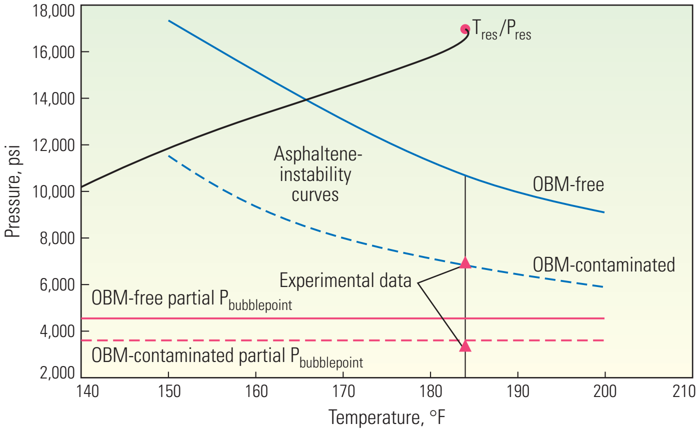


^ Modeling production conditions in the Hydro Gulf of Mexico commingling study. A schematic (*left*) shows the production system and nodes considered in the integrated production modeling of the study. Temperatures, pressures and compositions along the entire production system—28,000 ft in length—were evaluated by a molecular equation-of-state (EOS) model. Pressures and temperatures were calculated for the reservoir, borehole (BH), commingling zone, wellhead (WH) and separator over a five-year period (*right*). (Modified from Gonzalez et al, reference 33.)

contamination. The onset pressure for an uncontaminated sample was estimated by extrapolation to be 10,700 psi [73.8 MPa].

Simulation helped engineers understand how the oil and its asphaltenes would behave throughout production—from the formation to the wellbore and then, once commingled with condensate, to the surface. A molecular EOS model evaluated fluid at pressure, temperature and composition conditions along the 28,000-ft [8,534-m] length of the production system, and also predicted conditions at key locations through the first five years of the project (above).

Simulation results indicate that the black-oil reservoir fluid shows a high tendency to precipitate asphaltenes as the pressure decreases from its initial value of 16,988 psi [117 MPa] (right). This tendency is exacerbated as gas



^ Asphaltene-precipitation tendencies calculated for the Hydro commingling study. The pressure-temperature trajectory (black) of the fluid as it is produced from its initial temperature and pressure (red dot) intersects the asphaltene-onset pressure curve (solid blue) significantly above the bubblepoint pressure (red curve). This means the fluid has a high tendency to precipitate asphaltenes during production, and will probably precipitate them even if not commingled with fluids from the condensate reservoir. Experimental results on the oil sample, which was contaminated with oil-base mud (OBM), are shown as red triangles. Modeling calculated the asphaltene-instability curves for the OBM-contaminated sample (dotted blue curve) and for OBM-free oil. (Modified from Gonzalez et al, reference 33.)

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32. Du JL and Zhang D: "A Thermodynamic Model for the Prediction of Asphaltene Precipitation," *Petroleum Science and Technology* 22, no. 7 & 8 (2004): 1023–1033.
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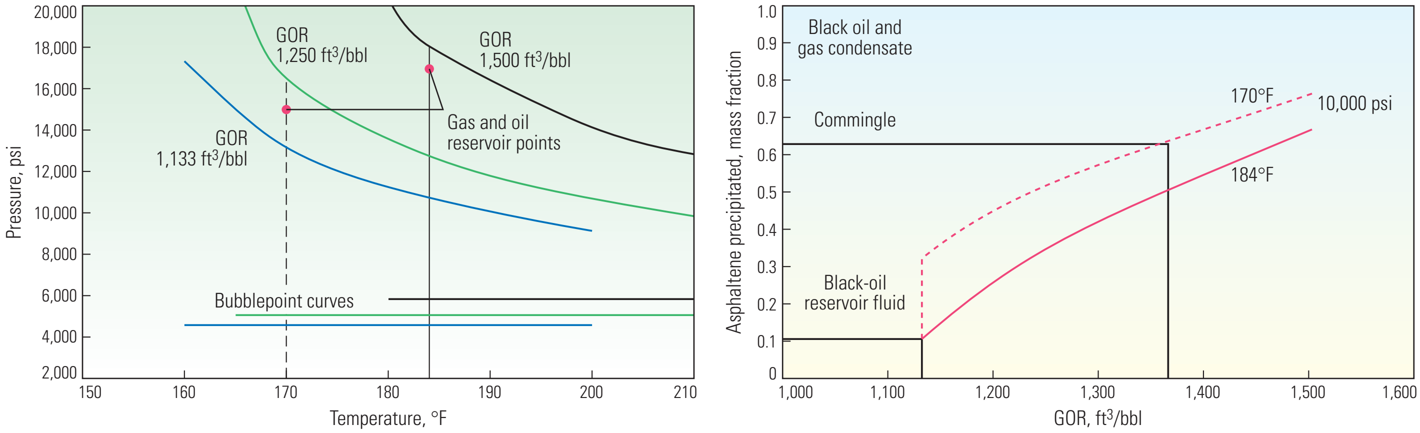


^ Changing asphaltene stability by commingling condensate with an asphaltene-prone oil. The addition of condensate (*left*) increases a black oil's gas/oil ratio (GOR), and increases the asphaltene-onset pressure. The asphaltene-onset curve of the original black oil (blue) is well below the oil reservoir's initial pressure and temperature. As GOR increases with commingled production, both reservoirs fall below the asphaltene-onset curves, indicating the likelihood of asphaltene precipitation in the wellbore. Another effect of increasing GOR is increased amount of asphaltene precipitation (*right*). A black oil with GOR of 1,133 ft^3/bbl [204 m^3/m^3] at reservoir conditions of 184°F [84°C] will precipitate 10% of its asphaltenes under depressurization to 10,000 psi (lower end of red line). At the lower-temperature conditions of commingling at 170°F [77°C] and 10,000 psi, GOR increases to 1,364 ft^3/bbl [276 m^3/m^3], and asphaltene precipitation increases to 60%. (Modified from Gonzalez et al, reference 33.)

condensate commingles with the black oil (above). The addition of condensate, which increases the gas/oil ratio (GOR) of the mixture, also increases the asphaltene-onset pressure. Without commingling, the black oil will precipitate approximately 10% of its asphaltenes under isothermal depressurization to 10,000 psi [69 MPa]. At the commingling conditions, with lower temperature and higher GOR, asphaltene precipitation increases to 60% at 10,000 psi.

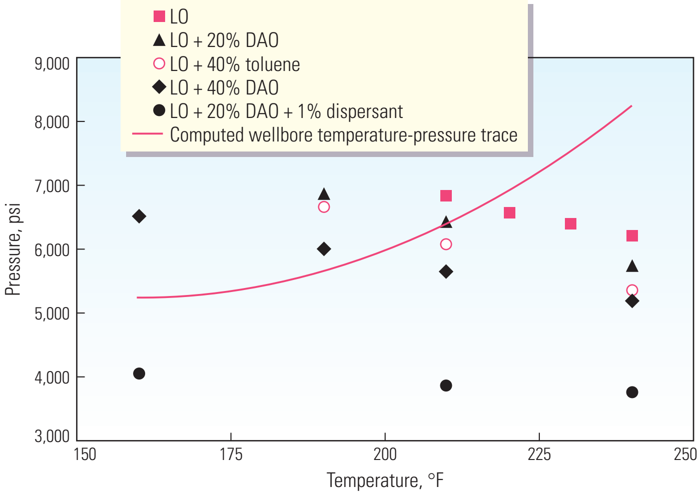
Since the asphaltenes showed a propensity for precipitation during primary depletion, injection of asphaltene-precipitation inhibitors was advised. It was also recommended that the layers be produced sequentially: first the oil layer, then the condensate layer, with no commingling.

South Kuwait's Asphaltenes

A combination of sampling, laboratory analyses and modeling also helped Chevron understand asphaltene behavior in the Greater Burgan field of South Kuwait, where asphaltene deposition on tubulars and flowlines posed serious challenges to reservoir management and production operations.[34] Fluid-analysis efforts centered on two objectives: characterizing the reservoir fluid to determine if asphaltene precipitation could be avoided, and evaluating solvents to mitigate production problems that could not be avoided.

For fluid characterization, four single-phase samples were collected from four wells in the Marrat carbonate reservoir interval. Oilphase-DBR engineers conducted intensive analysis of the sample from Well MG-OF4, and brief analysis of the samples from the other three wells. API gravity of the Marrat oils varied between 36° and 40°. SARA analysis on the live oil in Well MG-OF4 indicated 68.3% saturates, 11.2% aromatics, 18.4% resins and 2.1% asphaltenes. Results of gravimetric measurements on MG-OF4 oil determined asphaltene-precipitation pressure of 6,200 psi [42.7 MPa] and bubblepoint pressure of 3,235 psi [22.3 MPa] (next page).

Thermodynamic modeling treated the asphaltene as a solid phase in equilibrium with the reservoir fluid. Simulating fluid behavior over the range of conditions expected during production showed that precipitation of asphaltene from the Marrat oils could not be avoided, so engineers directed their search toward a cost-effective solvent for batch treatment or periodic injection to minimize deposition on tubulars and flowlines.



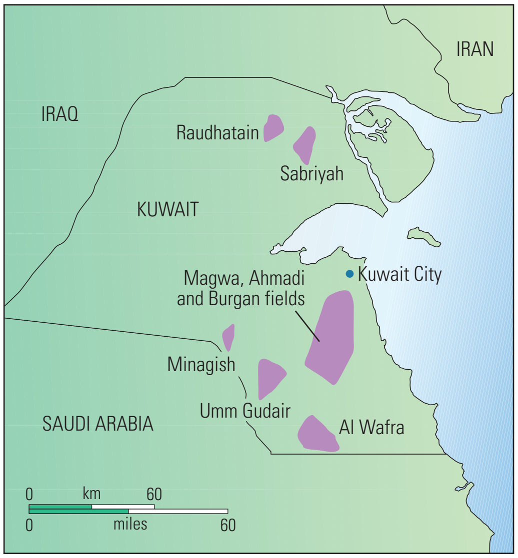
^ Using the acoustic-resonance technique (ART) to compare the ability of various solvents to dissolve asphaltenes. The ART helped determine asphaltene-precipitation envelopes of five solutions. These are, in order of increasing ability to keep asphaltenes in solution: live oil (squares), live oil with 20% deasphalted oil (triangles), live oil with 40% toluene (open circles), live oil with 40% deasphalted oil (diamonds) and live oil with 20% deasphalted oil and 1% dispersant (solid circles). (Modified from Kabir and Jamaluddin, reference 34.)

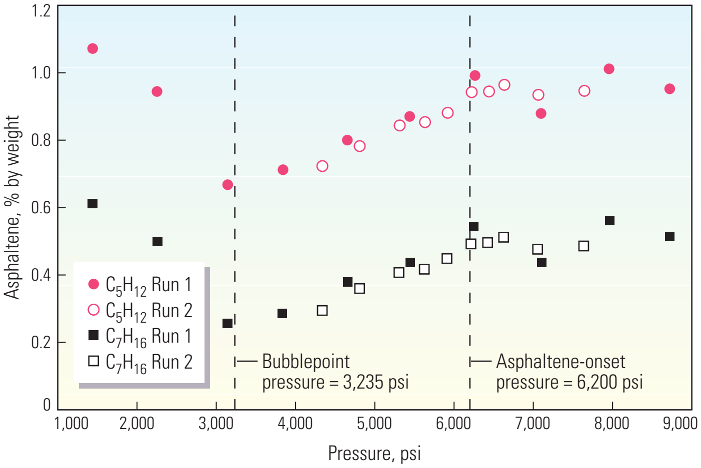
Because asphaltenes are by definition soluble in toluene, toluene has been used successfully as an asphaltene solvent in well interventions. However, restrictions imposed by regulatory organizations now require operators to use solvents that are more environmentally friendly.

As an alternative solvent, fluid analysts tested Marrat oil that had had its asphaltenes removed. For many oils, removal of asphaltenes by precipitation is a reversible process. Once asphaltenes have been removed by precipitation, the deasphalted oil has an increased capability to dissolve asphaltenes relative to the original live oil.

The first step in assessing the usefulness of Marrat deasphalted oil in resolubilizing its own asphaltenes was to remove the asphaltenes. This was achieved by dissolving the live oil in n-pentane to precipitate the asphaltenes, collecting the filtrate and evaporating the n-pentane. SARA analysis of this deasphalted oil (DAO) yielded 59.5% saturates, 25% aromatics, 15.3% resins and 0.2% asphaltenes—a reduction in asphaltene content of 90% compared with the live oil.

Using the acoustic-resonance technique described earlier, engineers compared the asphaltene-onset pressures of the live oil with those measured in solutions of live oil with varying amounts of added DAO (previous page, bottom). The live oil with 20% DAO by volume decreased the asphaltene-onset pressure by a small amount, and an additional 20% DAO reduced the onset pressure even more. The solution with 40% DAO was more effective than one with 40% toluene in decreasing asphaltene-onset pressure. However, the addition of 1% asphaltene dispersant improved the solvating power of the DAO even more significantly.





^ Gravimetric measurements on an oil from the Marrat formation of the Greater Burgan field in South Kuwait. The experiments began at pressures well above the reservoir pressure of 7,700 psi [53 MPa]. As pressure decreased to 6,200 psi, asphaltenes precipitated, indicated by the reduction in asphaltene content in the remaining fluid. The trend reversed at the bubblepoint pressure of 3,235 psi, when gas left the fluid. The concentration of asphaltene at the lowest pressure is higher than in the original oil because asphaltenes are more soluble in the degassed oil. Asphaltene content in the remaining fluid is determined by SARA fractionation, which can use different alkanes to precipitate asphaltenes. Asphaltene content precipitated by n-heptane [C_7H_{16}] is shown as black squares, and asphaltene content precipitated by n-pentane [C_5H_{12}] is shown as red circles. (Modified from Kabir and Jamaluddin, reference 34.)

While the results indicated that deasphalted Marrat oil might be able to dissolve Marrat asphaltenes in the laboratory, applying the technique in the field proved challenging. Deasphalting large volumes of oil with n-pentane was not feasible, so the procedure was modified to use condensate from a nearby gathering facility. The mixture was agitated and left at surface conditions to allow its lighter components to evaporate. Oil deasphalted in this way was nearly as asphaltene-free as that deasphalted by n-pentane, containing only 0.3% asphaltene by weight. However, reproducing the method at the well location was difficult, and the solution mixture pumped into the wellbore was only marginally deasphalted.

In spite of these difficulties, caliper measurements taken before and after treatment indicated that a substantial amount of asphaltene had dissolved from the borehole wall after a soak period of 24 hours. Not only was the treatment more environmentally friendly than other methods, but it cost approximately 50% less than using toluene.

Unfortunately, success was short-lived, because reservoir pressure continued to decline, and asphaltene remediation was required more often. Treatment frequency increased from once every three months to once a month until this part of the reservoir was shut down in 1998.

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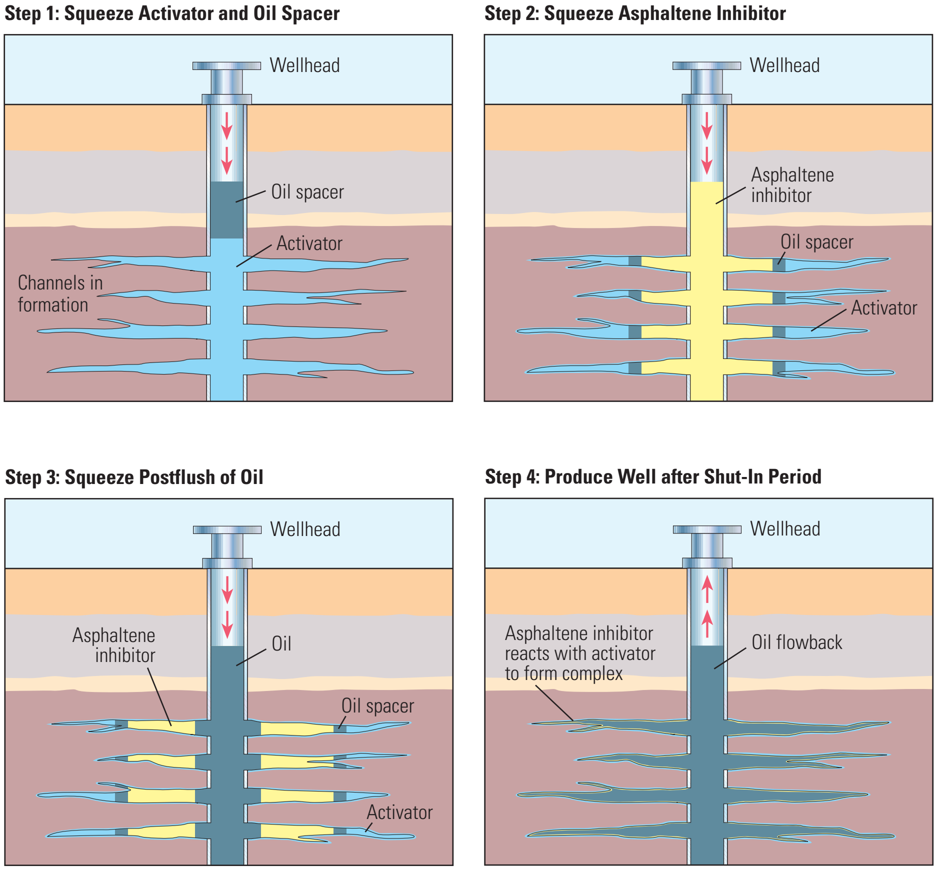

^ An optimized squeeze procedure for treating a formation with activator and asphaltene-deposition inhibitor. The first step entails cleaning out and flowing back the well, then pumping in activator and an oil spacer. The activator binds to the formation. In the second step, the precipitation-inhibitor chemical is injected. The third step comprises a postflush with crude oil, and in the final step the well is shut in for 12 to 24 hours, giving the activator and inhibitor time to form a complex before production begins. This method increases the residence time of the inhibitor in the formation. (Modified from Cenegy, reference 36.)

Preventing Formation Damage by Asphaltenes

Asphaltenes can deposit anywhere in the production system, but perhaps the most damaging place is in the near-wellbore region, where asphaltene-blocked pores are difficult to access for remediation. Conventional asphaltene flocculation-inhibitor treatments involve either periodic intervention with solvent soaks or continuous injection of chemicals into the wellbore. These methods are effective at preventing agglomeration and deposition of asphaltenes in flowlines and tubulars, but they do not protect the producing formation, because the chemicals interact with the oil after it has left the formation, potentially leaving asphaltenes behind.

An improved method developed by Nalco Energy Services adds chemicals to the crude oil while it is still in the formation.[35] The method entails squeezing an asphaltene-deposition inhibitor into the formation to stabilize the asphaltenes before flocculation occurs. However, tests have shown that squeezing inhibitor alone does not produce long-term benefits; formations do not absorb inhibitors adequately, allowing inhibitors to be quickly released from the formation as oil is produced. Pretreating the formation with an activator chemical enhances absorption of the inhibitor into the formation without changing formation wettability.

The general squeeze procedure includes cleaning out and flowing back the well, pumping in activator, a spacer of crude oil, inhibitor, and then more crude oil, and shutting in the well for 12 to 24 hours before resuming production (above).[36] The activator prepares the formation and reacts with the inhibitor to make a complex that remains in place for a prolonged period as the well produces oil.

Nalco has applied this method and related technologies in areas with some of the most serious asphaltene-deposition problems in the world, including Venezuela, the Persian Gulf, the Adriatic Sea and the Gulf of Mexico. In one example from eastern Venezuela, severe asphaltene-deposition problems caused a high-volume production well to plug within seven months of treatment.[37] Several cleaning methods had been attempted, including physically scraping the wellbore and injecting xylene down the tubing. Each cleaning event cost approximately US $50,000 and two days of shut-in production. After squeeze treatment with activator and inhibitor, the oil production rate increased and the frequency of well cleaning decreased to every eight months. The combination of increased production and less frequent cleaning generated an annualized gain of 60,882 barrels [9,674 m^3], and a return on investment of more than 3,000%.

Another case, this time from the Adriatic Sea, involved two deepwater subsea wells tying back to a floating production storage and offloading (FPSO) vessel. The operator learned of a potential asphaltene problem when the field was initially tested in 1993; examination of tubing strings revealed thick deposits of asphaltenes along a 3,300-ft [1,006-m] length of tubing, starting at a depth 6,500 ft [1,981 m] beneath the seafloor. Laboratory analysis of fluid samples indicated that asphaltene deposition could be controlled only by continuous downhole injection of asphaltene dispersant. The appropriate treatment program was designed and initiated with the desired results.

Once a successful treatment program was underway, additional laboratory work on samples collected as part of a monitoring program helped the operator optimize dispersant dosage. Dose-response curves were generated to guide field-treatment procedures and give the best economic balance between cost and the desired level of asphaltene control. It was clear from surface-sample analysis that as dosage increased, the volume of stable asphaltene dispersed in the crude increased. This indicated that fewer asphaltenes were available to deposit in the

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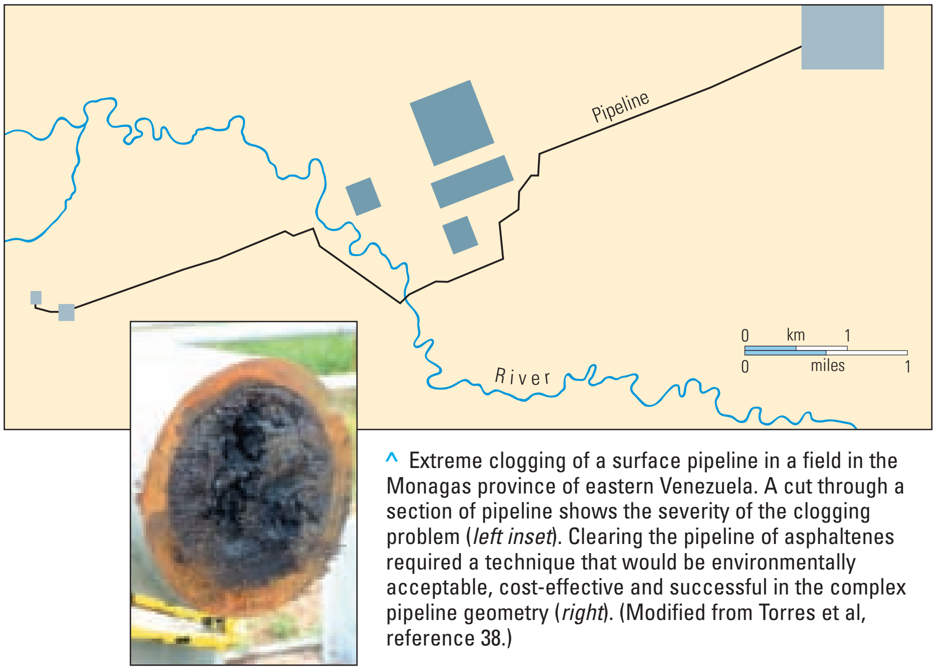
Asphaltene Deposition	Condition of Crude
0 to 1%	Crude strongly stabilized; dosage reduction indicated
1 to 2%	Crude well-stabilized; treatment adequate; no dosage change indicated
2 to 3.5%	Crude not perfectly stabilized; small increase in dosage indicated
> 3.5%	Crude not stabilized; insufficient dosage

^ Optimizing asphaltene-dispersant dosage in the Adriatic Sea. The volume of asphaltene deposition decreased as dispersant dosage increased. However, overtreating with dispersant increases cost. Optimization requires a compromise that allows a tolerable amount of deposition at a reasonable cost. A treatment level that allowed deposition of only 1% to 2% of the asphaltene volume enabled the wells to operate for several years without asphaltene-deposition problems. (Modified from Cenegy, reference 36.)



^ Extreme clogging of a surface pipeline in a field in the Monagas province of eastern Venezuela. A cut through a section of pipeline shows the severity of the clogging problem (*left inset*). Clearing the pipeline of asphaltenes required a technique that would be environmentally acceptable, cost-effective and successful in the complex pipeline geometry (*right*). (Modified from Torres et al, reference 38.)

^ Use of coiled tubing to clear an 8⅝-in. OD horizontal pipeline. Inclination of the injector-head frame allowed the CT to be injected into the clogged pipeline (*right*). Water and water-base gel helped to push out the organic solids (*left inset*). (Modified from Torres et al, reference 38.)

well (above left). A treatment level that optimized cost and sufficiently stabilized the asphaltenes was shown to provide a protection level that was 98% to 100% effective. Continuous treatment at this level has enabled the wells to operate for several years without any plugging problems.

Mechanical Removal of Asphaltenes

In a field in the northern Monagas province of eastern Venezuela, a combination of crude-oil composition and production conditions led to severe pipeline clogging by asphaltenes (above right).[38] During pipeline treatment, well production was temporarily diverted to a mobile testing unit, and the produced oil was transported by truck.

Flow testing determined that two pipeline sections totaling 9,300 m [30,513 ft] in length were completely plugged. Various cleaning options were considered, including high-pressure water blasting, steam and xylene injection, and pipeline pigging units. All were eliminated for technical, environmental and economic reasons. The other alternative, replacing the pipeline, would cost US $1.4 million and take eight months.

A team comprising specialists from the operating company and Schlumberger determined that 2-in. coiled tubing (CT) could potentially clear the 8⅝-in. outside diameter (OD) pipeline. An inclined injector-head frame allowed injection of the CT into the horizontally positioned pipeline. The coiled tubing entered the pipeline from five different entry points. Water and water-base gel were pumped to carry the dislodged solids, which came out in massive quantities (above). By using CT instead of other options to clean the pipeline, the client saved US $1 million and was able to return to normal operations more quickly.

The asphaltenes that returned to surface did not resemble asphaltenes typically precipitated in laboratory tests. Analysis of solid organic deposits in other fields in the region has shown that the solids are not pure asphaltene, but contain large amounts of other fractions. SARA fractionation of eight samples in one northern Monagas field averaged 16% saturates, 15% aromatics, 25% resins and 44% asphaltenes.[39]

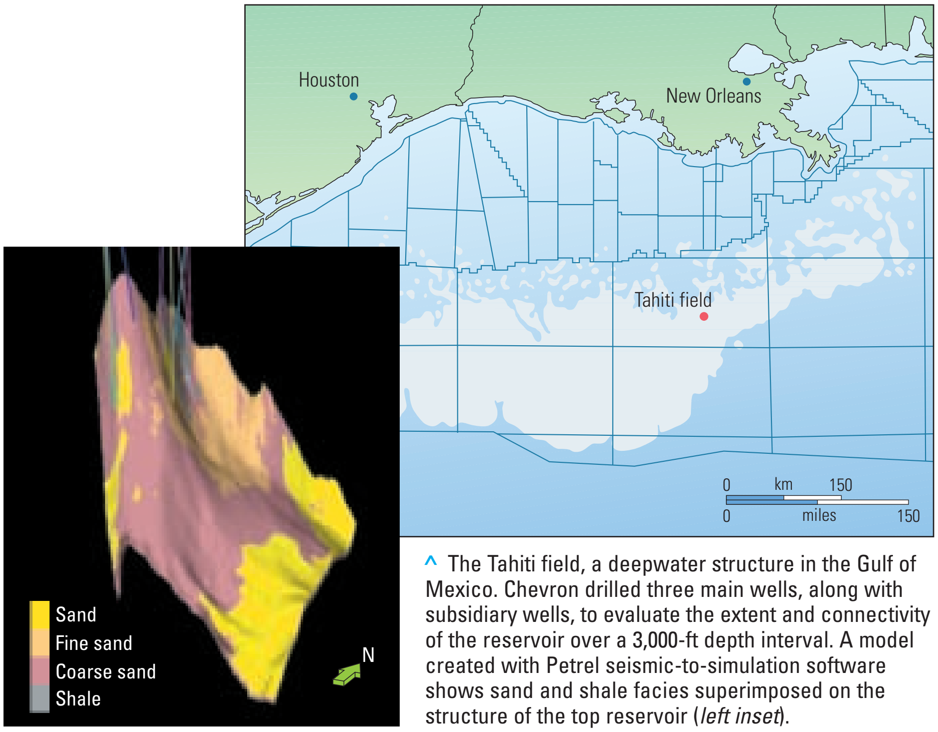
Making Use of Asphaltenes

Anyone who deals with asphaltenes in the oil field probably believes that the only positive value of asphaltenes in solution is that they have not yet formed an obstructive deposit. However, asphaltenes, like many other hydrocarbon components, have the potential to reveal important characteristics about the reservoir's fluid, history and connectivity.

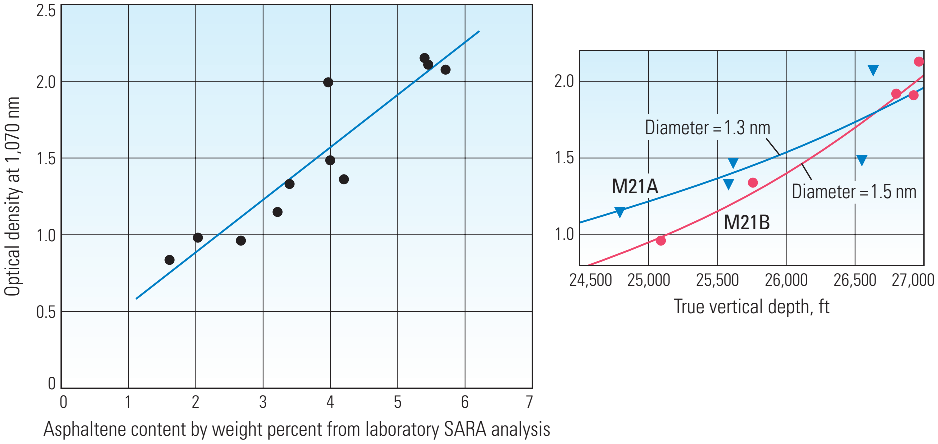
Chevron and Schlumberger used the optical properties of asphaltenes to understand reservoir connectivity in the Tahiti field, a deepwater structure in the Gulf of Mexico (left). The turbidite sands of the Tahiti field were discovered in 2002 in 4,000 ft [1,219 m] of water at true vertical depths ranging from 24,000 to 27,000 ft [7,315 to 8,230 m].[40] The reservoir layers dip steeply, having been tilted by salt tectonics. One appraisal well penetrated more than 1,000 ft [304 m] net of 600-mD pay. Field development is currently projected to cost US $3.5 billion.[41]

The cost of any development depends on the number of wells required for optimal recovery, which in turn depends on the number of reservoir compartments. To check for reservoir compartmentalization, Chevron performed downhole fluid analysis (DFA), which facilitates evaluation of fluid properties in real time. Downhole fluid analysis helps identify compartmentalization by using fluid-property signatures to determine whether fluids are in communication.[42]

Three wells, each with at least one sidetrack, intersected the main Tahiti reservoirs at different depths. Wireline optical spectroscopy tools collected fluid samples and analyzed optical density (OD) downhole at numerous depths spanning a 3,000-ft [914-m] interval. The high-quality OD measurements indicated significant change in hydrocarbon coloration with depth, implying a large variation in asphaltene content (left). Laboratory assessment by SARA fractionation revealed asphaltene content increases from 1.6% by weight at the top of the reservoir to almost 6% at



^ The Tahiti field, a deepwater structure in the Gulf of Mexico. Chevron drilled three main wells, along with subsidiary wells, to evaluate the extent and connectivity of the reservoir over a 3,000-ft depth interval. A model created with Petrel seismic-to-simulation software shows sand and shale facies superimposed on the structure of the top reservoir (*left inset*).



^ Downhole optical density (OD) varying with depth in the Tahiti field. Comparing downhole OD with laboratory SARA-fractionation results produces a linear relationship between OD and asphaltene content (*left*). Optical density measurements in the two main sands, M21A (blue) and M21B (red), show a clear increase in OD with depth (*right*). Furthermore, the measured optical densities, which are related to asphaltene concentrations, are consistent with solutions containing asphaltene particles that have 1.3-nm and 1.5-nm diameters in M21A and M21B, respectively. (Modified from Mullins et al, reference 11.)

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[45] While the origin of this belief is not well-documented, many books and papers make this assumption.

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[48] Kovscek AR, Wong H and Radke CJ: "A Pore-Level Scenario for the Development of Mixed Wettability in Oil Reservoirs," *American Institute of Chemical Engineers Journal* 39, no. 6 (June 1993): 1072–1085.

Yang and Czarnecki, reference 12.

[49] "Molecular Management," http://www.exxon.mobil.com/scitech/leaders/capabilities/mn_downstream_molecular.html (accessed July 30, 2007).

Saeger RB, Quann RJ and Kennedy CR: "Compositional Modeling of Refinery Streams and Processes," presented at the 232nd American Chemical Society National Meeting, San Francisco, September 10–14, 2006.

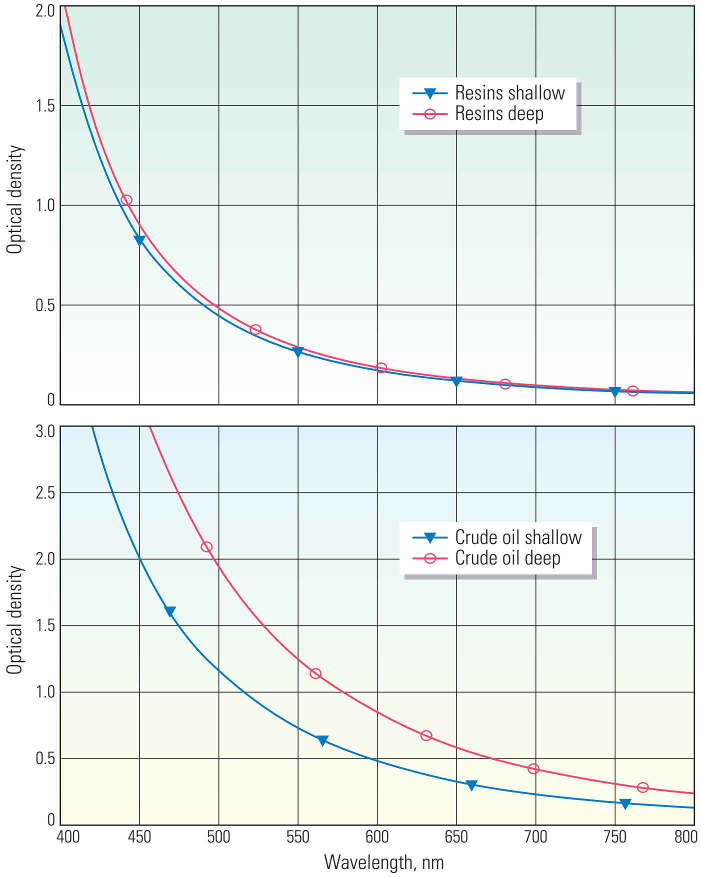
[50] Rodgers and Marshall, reference 4.

the bottom. The linear relationship between OD and SARA-fractionated asphaltene content proved that the variation in asphaltene content is the main cause of OD variation.

The best explanation for the continuous gradation in asphaltene content is a single, continuous fluid compartment whose asphaltenes have settled into equilibrium over geologic time.[43] This high degree of reservoir connectivity was good news for the operating company, because fewer wells will be required to develop this part of the field.

The OD measurements allowed reservoir specialists to incorporate fluid properties into an existing geological model over a large portion of the field.[44] The resulting model was used to predict the fluid properties, including asphaltene content, in a subsequently drilled well. The measured properties matched the predictions, confirming both the fluid model and reservoir continuity. The asphaltene content observed in the new well generally agreed with the large gradient seen in other wells.

A surprising result of further analysis of the Tahiti fluids is that resin content appears unrelated to asphaltene content (right). Asphaltene content indicated by OD measurements increases by more than 100%, while resin content increases by only 8% from the top to the bottom of the reservoir. This finding runs counter to a long-standing and widely held tenet that resins are associated with asphaltenes and are required for asphaltenes to be stable in crude oil.[45] Some asphaltene chemists have questioned this tenet, knowing that asphaltenes can be stable in toluene without resins.[46] Determining the role resins play, if any, in asphaltene stability may help chemists develop better methods for preventing and remediating asphaltene problems.



^ Resin and asphaltene optical signatures from shallow and deep crude-oil samples in the Tahiti field. In the original oils (*bottom*), where color is dominated by asphaltenes, the deep oil sample (red) has OD values that are twice those of the shallow sample (blue), indicating a large increase in asphaltene content with depth. After removing the asphaltenes by flocculation and precipitation, the remaining optical density can be attributed to resins. Resin content (*top*) shows little variation with depth in the reservoir. (Modified from Mullins et al, reference 11.)

More Work on Asphaltenes

Asphaltenes are best known for the problems they cause as solid deposits that obstruct flow in the production system. However, asphaltenes also cause other challenges to fluid flow: not only do they increase fluid viscosity and density, but they also stabilize oil-water emulsions.[47] Emulsions form when oil and water mix under conditions of agitation. Usually, the mixture is more viscous than its components, and flows less easily. Separating emulsified water and oil is difficult, and requires more than the gravitational methods used in most separators. A better understanding of the effect of asphaltenes may be the key to preventing the formation of emulsions or tempering the deleterious effects of these mixtures.

Asphaltenes are also an important factor in determining formation wettability (see "Fundamentals of Wettability," *page 44*). Changes in wettability can occur when even miniscule amounts of asphaltenes adsorb to formation grains. In some wettability models, the presence of asphaltene in the oil phase is required for the generation of oil-wetting conditions.[48]

Asphaltenes have the potential to derail upstream E&P activities, but they can also cause downstream disruptions, such as adhering to hot surfaces in refineries. (For more on refining, see "Refining Review—A Look Behind the Fence," *page 14*.) A more comprehensive characterization of asphaltenes and their properties is a priority for refiners, who hope to use molecular characteristics of asphaltenes and other hydrocarbon components in predictive compositional models for refining and blending.[49]

Hydrocarbons are among the most complex fluids on earth. A single heavy-oil sample may contain more than 20,000 chemical substances. The high resolving power and accuracy of new measurements, such as advanced mass spectrometry, allow for the identification of thousands of species in petroleum samples.

The way forward in asphaltene science relies on such techniques to better understand the structure and function of these complicated compounds. The current state of asphaltene and crude-oil characterization has been likened to a stage in the evolution of protein science; proteins were originally classified by solubility, but now, through the science of proteomics, their fundamental structure, in terms of amino acids, is understood. Similarly, the term "petroleomics" has been coined for the study of the structure of hydrocarbons.[50] The time will come when a crude oil will be characterized by all of its chemical constituents. —LS