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Digging Into Asphaltenes

Mass spectrometry uncovers chemical details of petroleum's most recalcitrant fraction

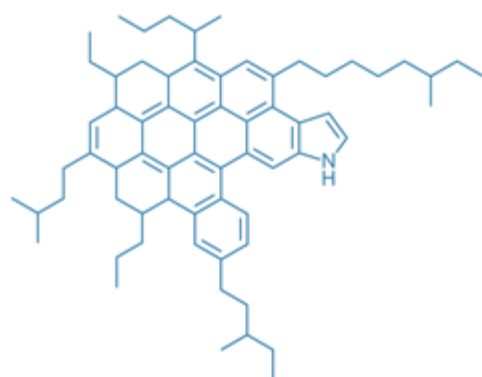
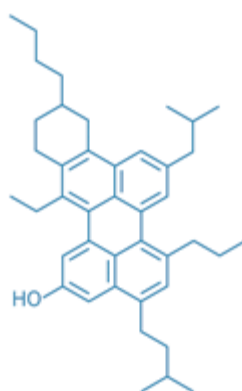
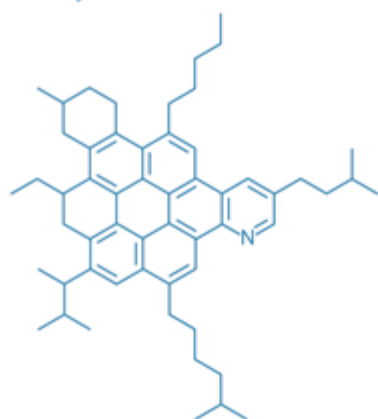
[Celia Henry Arnaud](#)



National High Magnetic Field

Laboratory

BIG GUNS National High Magnetic Field Laboratory's Amy McKenna (left) and Rodgers get the resolution they need to determine asphaltene composition from high-field Fourier transform ion cyclotron resonance MS.

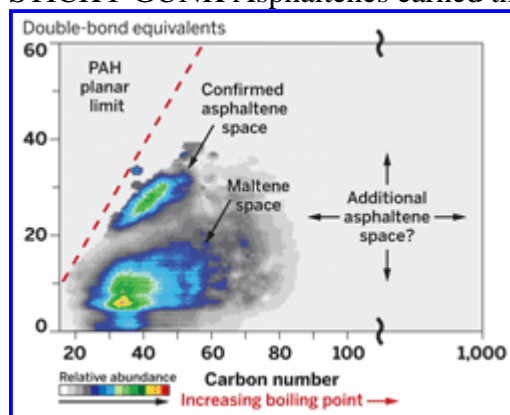


Proposed Structures Asphaltenes are a complex mixture that is thought to be rich in aromatic and -heterocyclic compounds, of which these are just a few examples.



Schlumberger

STICKY GUNK Asphaltenes earned the nickname “cholesterol of petroleum” by clogging pipes.



Courtesy of Ryan Rodgers

[View Enlarged Image](#)

PETROLEUM CONTINUUM This graph shows double-bond equivalents (DBE, rings plus double bonds) versus carbon number of compounds containing a single sulfur atom from all fractions of a Middle Eastern crude oil sample. Rather than concentrating at the extremes, petroleum components occupy all the composition space between the polycyclic aromatic hydrocarbon (PAH) planar limit and the aliphatic limit, which is where DBE = 0 along the horizontal axis. The asphaltene and maltene fractions are shown.

Petroleum remains a complex and poorly understood material, despite its importance and ubiquity in modern life. And perhaps no fraction of that black gold is less well understood than the fraction known as asphaltenes.

The name itself conjures the image of black, sticky gunk used to surface roads. And indeed, a primary use of this petroleum fraction is in road materials. But as the world's supply of easily accessed light petroleum for fuel and other uses dwindles, asphaltene-rich sources such as the Athabasca oil sands in Canada and the heavy oils of Mexico and Venezuela are growing in importance as substitute fuel sources.

Optimizing the value of these sources and converting them to something other than blacktop requires a molecular-level understanding of asphaltenes. Mass spectrometry is well suited to provide that deeper understanding of asphaltenes, and scientists are increasingly turning to that analytical technique to uncover the mysteries of this complex material.

One well-known fact is that asphaltenes have a tremendous effect on the physical properties of crude oil. “The way the viscosity of crude oil depends on asphaltene content is almost legendary,” says Andrew E. Pomerantz of [Schlumberger-Doll Research Center](#), in Cambridge, Mass., an oil-field services company that specializes in characterizing oil reservoirs. “Viscosity depends more than exponentially on asphaltene content.”

In petroleum refining, asphaltenes are often considered troublemakers. Because of their tendency to clog pipes, they have earned the sobriquet “the cholesterol of petroleum.”

Perhaps just as important, the high viscosity of asphaltenes causes them to clog underground rocks in oil-field reservoirs and impede oil extraction. "If the pipes get clogged, you can clean them out. If the rocks get clogged, there's almost nothing you can do," Pomerantz says. "If we could understand the composition of asphaltenes, the interactions within and between molecules, we could learn something that would allow us to predict when we will have problems with viscosity."

Some of the problems with characterizing asphaltenes originate from the outdated way of defining them: The asphaltene fraction comprises components that are soluble in toluene but insoluble in *n*-heptane or *n*-pentane.

The solubility definition is not a good way to describe asphaltenes, says [John M. Shaw](#), who studies petroleum thermodynamics at the University of Alberta, Edmonton. The only way to move beyond this 19th-century definition, he says, is to "develop models and understanding that are on a molecular basis."

Models must have sufficient detail "so you can optimize processes and squeeze every last drop of useful material from whatever fluid you're working with," Shaw says. "You need to be able to understand the fluid well enough to select the correct processes and to apply them in an optimized way."

People are turning to MS to provide that detail. With high-resolution MS, especially Fourier transform ion cyclotron resonance (FTICR) MS, scientists can determine the elemental composition of individual molecular species in asphaltenes. Tandem MS experiments can then reveal information about the structure of each component so identified.

To get an idea of how murky the picture has been, consider this: Until recently, scientists have had a hard time hammering down the molecular weight distribution of asphaltenes, perhaps the most fundamental of properties for such a complex mixture. Different methods have yielded estimates ranging from 500 daltons to more than 100,000 Da. The larger values have come from experiments performed with solvents that some researchers have found promote asphaltene aggregation. The biggest debates have been about these high estimates.

Among scientists who support the higher numbers is Alan A. Herod, an honorary research fellow at Imperial College, London. He maintains that current ionization methods underestimate the size of asphaltenes and that this fraction extends to at least 10,000 Da. He points out that because asphaltenes do not dissolve in the solvents used for some ionization methods such as electrospray ionization, it is likely that such techniques will miss high-molecular-weight species.

Herod and his coworkers have fractionated asphaltenes and examined the fractions with laser desorption MS. They think that fractionation by thin-layer chromatography or size-exclusion chromatography is the only way to access high-molecular-weight species. With size-based fractions on hand, it is possible to use different ionization conditions for low- and high-molecular-weight species. For example, matrix-assisted laser desorption ionization (MALDI) may be needed to look for species with higher masses.

The disagreement about the upper limits of asphaltene molecular weights is especially detrimental because molecular weight is critical in developing energy models for asphaltenes, Shaw says. "If you tell me the elemental composition and something about the molar mass," quantum mechanics can be used to predict "a complete energy model for any hydrocarbon," he says.

One stumbling block with using MS to answer questions definitively about asphaltenes has been the concern that some ionization methods may cause aggregation, fail to ionize some components, or break high-molecular-weight species into smaller pieces. But two recently developed MS methods appear to mitigate those concerns. Both indicate a high-molecular-weight limit significantly less than 10,000 Da.

The first is two-step laser desorption ionization MS (L^2MS), used by [Richard N. Zare](#) of Stanford University, Pomerantz, and coworkers (*J. Am. Chem. Soc.* **2008**, *130*, 7216). In this technique, an infrared CO₂ laser desorbs species from the surface by heating them enough to pop them off as neutral molecules but not enough to break them apart. An ultraviolet laser ionizes the intact molecules by exciting their aromatic rings, and the fragments are then mass analyzed. The researchers find a molecular weight distribution that peaks around 600 Da and extends to more than 1,000 Da.

"We have found it's very different when you do direct laser desorption ionization," Zare says of asphaltenes' molecular weight distribution. That method "leads to ion-molecule reactions and clustering. It gives much bigger weight distributions and has been known to give false signals," he says.

Corroborating these findings are those of [David H. Russell](#) and Chris Becker of Texas A&M University, working with Kuangnan Qian of ExxonMobil. They have shown that most species larger than 3,000 Da generated by laser desorption ionization are gas-phase aggregates rather than true molecular ions (*Anal. Chem.* **2008**, *80*, 8592). Their findings come from ion mobility MS ([C&EN, Sept. 15, 2008, page 11](#)), which separates ions on the basis of shape as well as charge.

Zare and Pomerantz plan to use L²MS to study interactions between asphaltenes and rock surfaces. These interactions affect properties such as the “wettability state,” which is the preference of rocks in the oil reservoir to contact one liquid, such as petroleum, rather than another, such as water. “A lot of people think that asphaltenes play a big role in determining the wettability state of a reservoir rock,” Pomerantz says. The team wants to measure flow properties through rocks and correlate them to surface chemistry characterized by L²MS. The information could be used to improve recovery of oil from reservoirs.

The second new method that is helping to settle the molecular weight question is laser-induced acoustic desorption (LIAD), utilized by [Hilkka I. Kenttämä](#) and coworkers at Purdue University (*Anal. Chem.* **2007**, *79*, 2688).

“The problem with mass spec has been that common ionization methods like MALDI and electrospray are highly selective and only ionize the most basic compounds,” Kenttämä says.

LIAD gets around this problem by evaporating asphaltenes as neutral molecules rather than ions. Kenttämä and coworkers deposit samples on titanium foil and fire a laser at the opposite side. The laser energy is converted to a sound wave that travels through the foil and pushes molecules off the other side. The molecules are then subjected to electron ionization, which nonselectively ionizes all organic compounds.

“We have evidence suggesting that we are desorbing and ionizing everything,” Kenttämä says. For asphaltenes, they find a molecular weight range of 400 to 1,100 Da, she says.

“If you know enough about the detailed organic composition of petroleum, you should be able to predict its properties and behavior.”

When they compare asphaltene samples from around the world, they find that molecular weight distributions vary depending on geographic origin. For example, Brazilian asphaltene samples have a lower molecular weight range than North American asphaltenes. “Once we have enough data, we need to start thinking about why the differences exist,” she says.

As a result of techniques such as L²MS, LIAD, and FTICR-MS, “the debate about the broad general range of molar mass has largely been resolved,” Shaw says. Measurements are converging to suggest that the mass of asphaltenes falls in the range of 500 to 2,000 Da.

With the molecular weight issue beginning to be resolved, the next goal is elemental analysis. [Alan G. Marshall](#)’s group at the National High Magnetic Field Laboratory at Florida State University is using high-resolution FTICR to push the molecular detail beyond just molecular weight. Coupled with atmospheric pressure ionization and electrospray ionization (especially with new reagents that extend ionization to nonpolar components), the instrument has such high resolving power that Marshall and coworkers can determine the elemental composition associated with each of more than 10,000 peaks in the mass spectrum.

In particular, they are using FTICR to bolster the model of heavy petroleum proposed two decades ago by chemist Mieczyslaw M. Boduszynski at Chevron (*Energy Fuels* **1987**, *1*, 2, and **1998**, *2*, 597). People had long assumed that because asphaltenes have high boiling points, they must be high-molecular-weight compounds. Boduszynski suggested that this need not be the case.

Boduszynski “laid out a very simple relationship between the different classes of compounds known to be in petroleum,” says Ryan P. Rodgers, a staff scientist at the [National High Magnetic Field Laboratory](#). “He pointed out how quickly boiling point goes up when you go from hexane to cyclohexane to benzene to pyridine to an aromatic amine. You get hydrogen bonding and intermolecular interactions that increase the boiling point. He backed it up with really nice field ionization mass spec results that showed that the heaviest crudes in the world contain no material over 2 kDa.

“High boiling does not equal heavy molecules,” Rodgers continues. “What it equals is aromatic molecules.” A high-boiling petroleum fraction is not one with a huge carbon number but instead one whose “aromaticity got big relative to the other species in crude oil,” he says.

Marshall, Rodgers, and coworkers have found that up to a carbon number of about 50, the components of petroleum occupy the entire compositional space between aliphatics and polyaromatic hydrocarbons. Rather than consisting of just low- and high-molecular-weight extremes with nothing between, petroleum is a continuum. When they graph the data as double-bond equivalents (DBE, the sum of rings and double bonds in a structure) versus carbon number, the components fill up the entire space. Their graphical analyses show that nonasphaltenes are relatively low in aromaticity but exhibit a wide carbon-number range and that asphaltenes have a similar carbon-number range but are high in aromaticity.

However, resolving even more components than they have identified already will require the use of FTICR with higher magnetic fields. “At 14.5 tesla, which is where we are now, we go up to 1,200 Da, and we’re pretty sure of everything in that range,” Marshall says. They hope to resolve species above that with a 21-tesla magnet.

“Our current results cannot discount asphaltenic species that lie in carbon number and DBE space beyond the highest-boiling maltenes,” Rodgers says. Maltenes are the components of asphalt or bitumen that are soluble in *n*-heptane and have a molecular weight range of 1,200 to 3,000 Da.

Marshall’s group also finds that asphaltenes tend to form noncovalent aggregates at concentrations as low as 0.1 mg/mL. This finding corroborates data from other methods such as diffusivity and fluorescence and suggests that aggregation is the natural state of asphaltenes in oil reservoirs.

The MS data show that the aggregates are made up of eight asphaltene monomers on average. The fact that each aggregate consists of only a few monomers is probably the result of attractive forces between the ring systems and repulsive forces on the periphery of the asphaltenes, says Oliver C. Mullins, an asphaltene expert who works for Schlumberger.

Knowing elemental compositions is not enough; identifying asphaltene’s chemical components is necessary, Marshall says. Several years ago, he coined the term “petroleomics” to describe the identification of petroleum’s chemical components. The petroleome is “like the genome or the proteome,” he says. “You can only talk about it when you can resolve all the component constituents. If you know enough about the detailed organic composition of petroleum, you should be able to predict its properties and behavior.”

Thanks to recent analytical studies, “the petroleome is becoming more and more defined,” Rodgers says. “We’re imposing aromaticity limits; we’re imposing heteroatom limits; we’re imposing molecular weight limits. The compositional space that petroleum occupies has shrunk considerably. Those boundaries make it a lot more defined system, which can make models based on our measurements and other measurements a lot better.” This may soon make it possible to be able to predict the actual value of oil bought and sold on the open market based on its composition, he says.

Ion mobility MS has potential for identifying the structure of asphaltene components, Russell says. Although high-resolution MS has proven to be the most informative tool for determining the elemental composition of asphaltene fractions, such data do not provide information regarding the structures of the compounds present, he says. Initial ion mobility MS data from Russell and Becker show considerable promise for attaining a better understanding of the molecular structures present in asphaltene.

A better chemical understanding of asphaltenes may also help improve recovery of oil from reservoirs, Mullins says. Although MS is unlikely to be used in the field, it can provide compositional information that can be combined with spectroscopic measurements made in the field.

“Enhanced oil recovery is going to loom as a more important player in the oil business,” Mullins says, because current extraction techniques often leave 70% of a field’s oil in the ground. “If you could get even a minor fraction of that stuff out, it’s a lot of oil,” he says, and better compositional and spectroscopic data could help.

For example, the asphaltene content at various spots in an oil field can determine how difficult it would be to develop that reservoir. “What we’re looking for in the subsurface is a continuous distribution of asphaltenes,” Mullins says. A continuous distribution implies that various portions of a reservoir are connected and the petroleum would be easier to remove. A discontinuous asphaltene distribution suggests that the petroleum is in isolated pockets that must be tapped separately.

“If the reservoir is like a kitchen sponge, where all the cells are connected to each other, you can drain the reservoir with relatively few wells,” Mullins continues. “If the reservoir is like a spool of bubble wrap and your well is like a needle, you drain small compartments but you don’t drain the entire spool. If you don’t know it, you can have billion-dollar mistakes in a single field.”

One way to improve recovery is to change the wettability of the rock in the geologic formation surrounding the oil. “If the rock is oil-wet, it holds on to the oil and won’t give it up,” Mullins says. “Enhanced oil recovery comes down to surface science, and the asphaltenes are key players.” If you don’t know the molecular structure, you won’t be able to optimize recovery as effectively, he notes. And as Pomerantz says, “We get a lot of energy from oil, and we’re moving to oil sources that are asphaltene-rich, where these issues are only going to become more important.”

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