Phase Behavior of Heavy Oils and Bitumen

Dr. John M. Shaw is a specialist in the phase behavior of hydrocarbons—from coal liquids and heavy oils to condensate-rich reservoir fluids—and the mixing and demixing issues related to them.

Dr. Shaw leads the Petroleum Thermodynamics Research Group, in the Faculty of Engineering at UoA.

Investigating phase behavior
It is difficult to study and understand the phase behaviors of heavy oil and bitumen and their constituents. These asphaltene-rich fluids are opaque to visible and infrared light, and contain nano- or microdispersed phase domains. The X-ray transmission tomography technology developed by Dr Shaw permitted the first direct observation of the phase behavior of opaque asphaltene-rich fluids. Dr Shaw says the UoA has subsequently “cornered the market” in investigating the phase behavior of heavy oils under refining and production conditions using X-ray PVT measurements.

Over time, a key limitation with the X-ray transmission tomography technology has become apparent. Used on its own, dispersed phase density, volume fraction, phase state (solid or liquid) and particle or drop size are not readily discriminated. The solution is to combine X-ray PVT with rheology, nanofiltration, small-angle X-ray scattering (SAXS) and calorimetry measurements. This is time consuming but, according to Dr Shaw, the results are impressive. Only a few years ago most researchers considered heavy oil to be a single-phase Newtonian fluid. With this combination of techniques, three and four phase regimes are readily identified—particularly at reservoir and sea-bottom conditions, where the multiple phases lead to shear thinning and other non-Newtonian rheological properties.

Composition gradients
Fluids in heavy oil and bitumen reservoirs are not homogeneous. They typically exhibit gradients from heavy to light between the bottom and top of a compartment. When materials such as CO₂ and light hydrocarbons are injected, these gradients facilitate horizontal and upward movement in preference to downward movement. Understanding compositional gradients and their impacts on phase behavior and transport properties are critical inputs for exploitation technology selection, and reservoir modeling and management tasks. Local diffusion and permeability calculations are particularly sensitive to phase behavior and composition.

Combining experimental techniques
The Petroleum Thermodynamics Research Group combines information from differential scanning calorimetry (DSC), temperature-modulated differential scanning calorimetry (TMDSC), rheometry, small-angle X-ray scattering (SAXS), X-ray PVT, densitometry, and other experimental techniques. Combined with the best available theories, the aim is to determine the temperatures and enthalpies of phase transitions, the state and number of phases, and the reversibility of phase transitions observed. Studies begin with native oil samples that are partitioned physically, without the addition of solvents, by nanofiltration, atmospheric and vacuum distillation, if and when required.

Understanding mixtures
Heavy oils and bitumen may comprise two liquids and vapor (LLV), and solids. For mixtures exhibiting LLV phase behavior, addition of miscible or immiscible components, such as CO₂, light oil or water, as envisioned in numerous production schemes, shifts the pressure and temperature of the multiphase behavior. For example, under some conditions, even mixtures of methane and hexane exhibit LLV phase behavior. With the addition of ethane, miscible with both methane and hexane, the LLV behavior moves to higher pressures and temperatures and disappears with the addition
of sufficient ethane. By contrast, adding nitrogen shifts the LLV behavior to lower temperatures and higher pressures and makes it larger. Consequently, the phase behavior of closely related mixtures can differ radically at fixed temperature and pressure. Small changes in diluents or injection fluid composition or mass fraction can have a huge impact on phase behavior outcomes. This in turn affects production and refining process outcomes—for better or worse.

**Diluents and temperature**
Some results are surprising and counter-intuitive. For example, oil and water do mix, and do so in a significant way at temperatures above 330 degC where hydrocarbons can dissolve up to 30% water. Steam assisted gravity drainage (SAGD) production systems operate with local maximum temperatures exceeding 250 degC, where water solubility is an order of magnitude or two lower. Envisioned electrical heating systems for reservoirs, designed to refine the hydrocarbons in situ, can easily exceed 330 degC locally, as can temperatures used in refining. This means that, for numerous high-temperature applications, water could be preferred to light or lighter hydrocarbons as an additive or diluent. By contrast, in low-temperature reservoirs, the addition of CO2 is likely to result in changes in phase behavior that are detrimental to production.

**Implications for production and refining**
A better understanding of the phase behavior of heavy oils is essential to avoid mistakes in the efficiency and safety of production and refining systems. It is necessary to understand the equilibrium and transport properties of these materials from the molecular to the meter-length scales. The economic impact of inadequate understanding can be huge. “How can a refiner price available crudes accurately without understanding their constituent molecules and the products that can be produced from them?” asks Dr Shaw. Reducing pressure in a reservoir can cause deposition of solids that kill production. Similarly, multiphase behavior can cause problems such as the deposition of coke during refining. Dr Shaw considers that commercially available simulators do not handle solid hydrocarbons, and they do not model the phase behavior of heavy oils or their constituents, particularly at low temperatures. The work ongoing at the UofA is leading to a better understanding of the properties of bitumen and heavy oil and the provision of accurate data and computational tools for process simulators of the (hopefully) near future.

Dr Shaw cites the mixing of light hydrocarbons with bitumen at room temperature as an example of the importance of understanding the details of phase behavior in designing a refining process for bitumen. In the process bitumen is mixed with light hydrocarbons. If mixing causes heat, evaporative loss of the light hydrocarbons is excessive and a cooler must be added to the process. If mixing causes cooling, then bitumen recovery levels drop, and a process heater must be added. As these processes operate at a large scale, the CAPEX and OPEX uncertainties introduced by commercial simulators, which yield both results with minor changes in assumptions, is significant. Research at UofA, indicates that the actual behavior of such mixtures depends on the thermal history of the bitumen, which reinforces the importance of the work at UofA in building a knowledge base.

**The importance of better planning**
There are several examples of inefficient heavy oil production systems design from around the world. One such example relates to the Lloydminster region in Canada, where primary production has historically recovered about 5–10% of the reserves in place, using standard drill and pump technology. In some areas, the remaining heavy oil (90–95%) has been abandoned and secondary recovery is difficult because the reservoirs have been depressurized and damaged by excessive, and in some cases unrecorded, drilling. Thirty percent or more of the oil is sold under reservoir conditions. Dr Shaw considers the production methods
employed to be “almost criminal,” when he believes that simply heating the reservoir to around 50 to 60 degC would have made production far more efficient and recoveries significantly greater.

The work of the Petroleum Thermodynamics Research Group at UofA, under the leadership of Dr Shaw, will enable better planning of future production and refining systems for heavy oil. The group welcomes opportunities to work with new sponsors and organizations involved with heavy oil research. For more information visit their UofA Web site.

About John Shaw

Dr John M. Shaw is a specialist in the phase behavior of hydrocarbons—from coal liquids and heavy oils to condensate-rich reservoir fluids—and the mixing and demixing issues related to them. Dr Shaw obtained his BA Sc (1981) and PhD (1985) at the University of British Columbia. These qualifications were in chemical engineering and metallurgy and materials science, with a particular focus on catalysts for coal-to-liquids processes. During his PhD studies, he became interested in the organic side of the chemical reactions, determining that some of the outcomes must be related to multiphase behavior.

Dr. Shaw served as professor in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto before joining the University of Alberta (UofA) in 2001. He developed the X-ray view cell technology that permitted the first direct observation of the phase behavior of opaque asphaltene-rich fluids. He has held visiting professorships at the Technical University of Delft (TU Delft), the Netherlands; the Institut Français du Petrole, France; and the Syncrude Research Centre, Canada. He has delivered invited lectures at numerous conferences, institutes, universities, and private companies; sits on the network coordinating council for the Canadian Oil Sands Network for Research and Development (CONRAD), and is an associate editor of Energy and Fuels. Dr Shaw acknowledges the insights he has gained through mentors in leading academic institutes such as the TU Delft and companies such as Amoco and Imperial Oil.

Dr Shaw says that, for the first 20 years of his career, oil prices were too low to attract much interest from industry in research on the phase behavior of heavy oil. His appointment in 2001 as the NSERC/AERI Industrial Research Chair in Petroleum Thermodynamics at UofA, and the subsequent high level of industry support for its activities, reflects the growing recognition that heavy oil is now an increasingly important global energy source.

The Petroleum Thermodynamics Research Group

Dr. Shaw leads the Petroleum Thermodynamics Research Group, in the Faculty of Engineering at UofA. The group investigates the phase behaviors of reservoir fluids, heavy oils, and bitumen, providing knowledge to improve emissions and the cost-effectiveness of producing, refining, and transporting these resources. The group is funded by the Alberta Energy Research Institute (AERI) and the Natural Sciences and Engineering Research Council of Canada (NSERC). Industry sponsors include oil companies and service companies, who bring challenging operational problems for the group to solve, and opportunities for applying new technologies and ideas developed at the UofA. Under the leadership of Dr Shaw, the group strives to engage people at all levels. Current participants range in age from 16 to 60. Group members come from around the world, including Canada, Venezuela, Belarus, China, Nigeria, and Iran. The group typically comprises 15 to 20 people, including PhD students, post-doctoral fellows, visiting scientists and engineers, research engineers, and undergraduate summer and co-op students. Female high school pupils get actively involved through the UofA’s Women in Scholarship, Engineering, Science, and Technology (WISEST) program.