Downhole Fluid Analysis Coupled with Novel Asphalte Science for Reservoir Evaluation

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ABSTRACT

In elementary school science, one learns that matter is composed of solids, liquids and gases. True to form, crude oils obey this basic tenet with constituent solids (asphaltenes), liquids, and hydrocarbon (and other) gases. Modeling of gas-liquid properties of reservoir crude oil such as gradients of GOR, saturation pressure, etc. can be accomplished using standard cubic equations of state (EoS). Moreover, the new technology downhole fluid analysis (DFA) enables measurement of these corresponding gradients of reservoir fluid properties. When these DFA-measured fluid gradients are shown to be in equilibrium, that is, properly modeled by a cubic EoS, then reservoir connectivity is implied. Equilibration of reservoir fluids requires massive fluid flow throughout the reservoir and is inconsistent with intervening sealing barriers.

In contrast, modeling the solid-fluid equilibria of reservoir crude oils had been precluded until now because of the lack of understanding of asphaltene fundamentals. For example, there had been a ~6 orders of magnitude debate about asphaltene molecular weight. Without knowing the asphaltene size, gravity and other terms cannot be determined and proper asphaltene modeling in reservoir crude oils is precluded. Major advances in asphaltene science have been made, codified in the modified Yen model and are based on extensive laboratory and oilfield studies. This new understanding enables proper modeling of solid-fluid equilibria of asphaltenes correcting perhaps the greatest limitation of petroleum science. Using DFA-measured asphaltene (and GOR) gradients coupled with this new asphaltene nanoscience, it is now possible to model heavy-end distributions of reservoir fluids from heavy oils to condensates.

Moreover, for low GOR crude oils, the GOR is homogenous; thus, only the heavy end gradients are useful for reservoir connectivity analysis. The new technology of DFA coupled with new asphaltene science is shown in numerous case studies to greatly broaden the understanding of reservoir crude oils and represents a powerful new tool to address reservoir connectivity.

INTRODUCTION

The reservoir remains the single biggest technical uncertainty in the oil business; yet billion dollar decisions are based on practically efficient but highly deficient understanding of the reservoir. Reservoir compartmentalization, and more importantly, reservoir connectivity remain difficult to discern. Pressure communication is a necessary but insufficient condition to establish flow communication (connectivity).[1] Traditional geochemical analyses have been partially effective in the identification of compartmentalization, but are inadequate for predicting reservoir connectivity. Indeed, bad news of compartmentalization is much easier to obtain than possible good news about reservoir connectivity. New methods are needed to address this most important risk factor, reservoir connectivity.

Reservoir fluid distributions can be used to address reservoir connectivity. As will be discussed below, these reservoir fluid distributions are readily measured by DFA. Stair-step discontinuous distributions of reservoir fluids indicate the presence of sealing barriers (thus compartmentalization).[1-4] In particular, if a more dense fluid is found higher in the column, a permeability barrier is strongly implied.[1-4] Likewise, the accumulation of higher density components, asphaltenes, higher in the oil column, indicates a permeability barrier, even at nominally identical overall fluid densities.[1,3] Any chemical analyte whether
In contrast, a continuous distribution of fluid properties in a reservoir can indicate (but not prove) connectivity. In one example, a large influx of biogenic methane into a black oil column gave rise to a large continuous gradient of GOR and methane isotope ratios among other properties. Continuous large fluid compositional gradients especially from current dynamics (such as current reservoir charging) are inconsistent with the presence of intervening sealing barriers, thus indicating connectivity.

In particular, if the reservoir fluids are in equilibrium, then it is a stronger indication of connectivity because to achieve equilibrium, there must be sufficient fluid flow continuity. In contrast, a relatively small amount of flow connectivity is required for pressure equilibration. For example, Fig. 1 shows a large GOR gradient measured by DFA; the equilibrium gradient is indicative of vertical connectivity.

In general, different hydrocarbon fluids charge into reservoirs over long times. In a normal burial sequence, lighter hydrocarbons enter the reservoir at later times. The evolving distribution of reservoir fluids cannot reflect a state of fluid equilibrium immediately after charging has terminated. Frequently, reservoir fluids are found in grossly nonequilibrium conditions reflecting this charge history. Equilibration then requires massive fluid flow in the reservoir. Diffusive mixing, which is extremely slow, is required in most equilibration processes. And a sealing barrier or low transmissivity fault would preclude equilibration. Nevertheless, connectivity is difficult to establish, and all fluid parameters must be considered in conjunction with other data in order to fully probe reservoir connectivity.

FUNDAMENTALS OF ASPHALTENE SCIENCE

The question naturally arises – “what about modeling the heavy ends?” Asphaltenes, the heaviest and most aromatic component of crude oil had been the subject of much debate. Incredibly, there had been a debate regarding asphaltene molecular weight that spanned up to 6 orders of magnitude. Without knowledge of asphaltene fundamental properties, a first principles approach to modeling asphaltene gradients was precluded. Inclusion of a gravity term is required for modeling reservoir fluids. For gravity, size counts, so without knowing the molecular or colloidal size of asphaltenes, modeling asphaltenes in reservoirs was reduced to fitting with pseudo components. In particular, cubic equations of state (EoS) are all variants of the Van der Waals EoS, a derivative of the ideal gas law. Cubic EoS were developed for gas-liquid equilibria and were never intended to handle solids, let alone complex solids such as asphaltenes. Obviously, an approach born out of the ideal gas law is not likely to work for solids. For example, pseudo components in a cubic EoS require their critical point temperature and pressure, the conditions where gas and liquid phase properties are identical. Asphaltenes do not have a gas phase, nor a liquid phase thus do not have critical constants.

Here, we try to lend credence to the assertion about the (former) inability of petroleum science to address asphaltene gradients in reservoirs. Almost the entire readership of this paper has heard of the Peng-Robinson equation of state, developed in 1976. But a small fraction of the readership has ever heard of the Yen model of asphaltene science, developed in 1967. But the Yen model has dominated the thinking in asphaltene science for 40 years! Why has this readership not heard of this long-standing asphaltene model? Because the Yen model is worthless for reservoir evaluation. The Yen model found great utility in the analysis of phase separated, solid asphaltenes; but it did not stipulate the molecular or colloidal size of
asphaltenes, the gravity and other terms remained unknowable, so the Yen model could not be used to evaluate asphaltene gradients. Fig. 2 shows a schematic of the Yen model of asphaltene science.

Figure 2. The Yen model [18] of asphaltene science.[16,17] Different chemical moieties of asphaltenes are identified, but the specific asphaltene structures in crude oils are not identified.

Many, fundamental advances have taken place heralding a renaissance in the field of asphaltene science.[13,19] These advances have enabled identification of the asphaltene structures in crude oils, from (movable) heavy oil to light oils; these developments have been codified in the “modified-Yen model”. [13] Fig. 3 shows the asphaltene structures germane to reservoir evaluation.

Figure 3. The modified Yen model [13] stipulates the molecular and colloidal structures found in crude oils. Nanoaggregates have ~6 molecules and clusters have ~8 nanoaggregates. Condensates have a molecular dispersion of heavy ends, stable black oils have asphaltenes in nanoaggregates and unstable black oils and heavy oils have at least some asphaltenes in clusters.

Numerous laboratory case studies and DFA field studies have proven the validity of the modified Yen model.[13] The molecular form of asphaltenes – the left most structure in Fig. 3 – is found only in condensates. Indeed, it is really a dispersion of the heaviest resin molecules that are similar to asphaltenes (they imbue color to the condensates). For stable black oils, asphaltenes are dispersed as nanoaggregates – the center structure in Fig. 3. And in heavy oils, the asphaltenes are dispersed as clusters – the right most structure in Fig. 3. In some cases, a mixture of structures is found. For example, in unstable black oils, a mixture of nanoaggregates and clusters is found. Consequently, there is some ambiguity in modeling asphaltene gradients. The recommended procedure is to measure both the asphaltene and GOR gradients with DFA. As discussed in the next section, GOR gradients must be determined to understand asphaltene gradients. With both the asphaltene and GOR gradients measured, the molecular or colloidal dispersion of asphaltenes is obtained, thereby greatly increasing the understanding of the oil column and corresponding implications for the reservoir.

THEORETICAL FOUNDATIONS OF ASPHALTENE GRADIENTS

There has been a great deal of work modeling the phase behavior of asphaltenes.[20,21] In particular, the Flory-Huggins polymer theory has been employed to model asphaltene phase behavior with the idea that the asphaltene species of interest are much larger than the solvent molecules.[20,21] Here, we are interested in asphaltene gradients. Nevertheless, a theoretical formalism used for modeling asphaltene phase behavior, the Flory-Huggins formalism, can be extended to model asphaltene gradients by inclusion of the modified Yen model.[22,23] The great promise of this approach is that a single formalism can then be used to model both asphaltene gradients and their phase behavior. This work is in progress.

With the size and identity of the asphaltene species in crude oil understood within the context of the modified Yen model, asphaltene gradients can be modeled from first principles. The Gibbs free energy $\Delta G(h)$ of the asphaltenes in the reservoir crude oil can be expressed as a sum of free energy of three terms; gravity, solubility and entropy.[22]

$$\Delta G(h) = \Delta G_{\text{grav}}(h) + \Delta G_{\text{sol}}(h) + \Delta G_{\text{ent}}(h)$$  \hspace{1cm} (1)

Gravity must be included when modeling fluids in reservoirs (unlike most laboratory studies).
because large vertical reliefs are routine. The gravity term is fairly simple and is based on basic tenets. Archimedes buoyancy (in use for two millennia) gives the energy required to ‘lift’ the asphaltene particle of volume \( V \) with gravity \( g \) to a height \( h \) above the lowest point in the oil column. This energy depends on buoyancy \( V \Delta \rho \) (which has the units of mass) where \( \Delta \rho \) is the density contrast between asphaltene and the continuous liquid phase. For a homogeneous liquid column, Eq. 2 gives the gravity term [22].

\[
\Delta G_{grav}(h) = V \Delta \rho g h \tag{2}
\]

Many black oils are low GOR; thus Eq. 2 applies (as discussed below). To obtain the ratio of the concentration of asphaltene \( C_A \) at height \( h \) relative to the lowest point in the oil column (\( h=0 \)), the Boltzmann factor (Eq. 3) is used with the gravitational energy (Eq. 2) being in the argument of the exponential.[22]

\[
\frac{C_A(h)}{C_A(0)} = \exp \left( -\frac{V \Delta \rho g h}{kT} \right) \tag{3}
\]

where \( k \) is Boltzmann’s constant and \( T \) is temperature. This Boltzmann equation has been one of the foundations of statistical mechanics for a century. For a fluid (liquid) phase that varies with depth, for example, if there is a GOR gradient, then the fluid density is not constant with height and an integral form of Eq. 2 must be used.[22]

Eq. 3 shows that as the asphaltene species get larger, then the gravity term produces larger gradients. Thus, for a molecular dispersion of asphaltene-like heavy resin molecules (left most species in Fig. 3), the gravity term is not large. For nanoaggregates (center, Fig. 3), the gravity term is moderate. For clusters of asphaltene nanoaggregates (right, Fig. 3) the gravity term is large.

A second important consideration is the solubility of asphaltene in the liquid phase.[20-23] Asphaltenes are not soluble in light alkanes. Indeed, asphaltenes are defined to be insoluble in n-heptane.[17,19] Asphaltenes are insoluble in CH\(_4\); correspondingly natural gas is colorless. The key point is that asphaltenes are only sparingly soluble in high GOR crude oils and are much more soluble in low GOR crude oils. Figure 4 shows this pictorially. The lack of asphaltene solubility in high GOR fluids is well known in production. Injection of CH\(_4\), separator gas, or CO\(_2\) into black oil can cause a phase separation of an asphaltene rich phase. The same applies to reservoir crude oil columns.

Equation 4 gives the free energy of the solubility term \( \Delta G_{sol} \) in terms of asphaltene and maltene solubilities (here, maltene is the live crude oil minus asphaltene).[20-23]

\[
\Delta G_{sol} = n_m \phi_A V_A (\delta_A - \delta_m)^2 \tag{4}
\]

Where \( n_m \) is the number of moles of maltene, \( \phi_A \) is the volume fraction of asphaltene, \( V_A \) is the molar volume for the relevant asphaltene species (cf. Fig. 3). The solubility parameters \( \delta_m \) and \( \delta_A \) essentially give the interactive chemical energy density of the maltene and asphaltenes respectively. Asphaltenes have a very high solubility parameter and light hydrocarbons like methane have a very small solubility parameter. A large mismatch in the solubility parameters gives a large reduction in solubility.

Figure 4. Left. Light alkanes such as CH\(_4\) flocculate asphaltenes leaving a lightly colored fluid phase. Asphaltenes have little solubility in high GOR fluids. Right. Asphaltenes have appreciable solubility in low GOR crude oils.

If there is a large GOR gradient, then the crude oil at the top will have low asphaltene content compared to the crude oil at the bottom of the column. That is, large GOR gradients will drive large asphaltene gradients due to the solubility term. This effect magnifies viscosity gradients. The top of the column would be high GOR, low asphaltene – thus low viscosity. The bottom of the column would be low GOR, high asphaltene content – thus high viscosity.

The third term to be considered for asphaltene gradients is the entropy term.[20-23] The Flory-Huggins entropy term \( \Delta G_{ent} \) is given in Eq. 5 and is seen to be closely related in form to the entropy expression from the ideal gas law, but adapted for polymers.
\[ \Delta G_{\text{end}} = kT(n_i \ln \phi_m + n_A \ln \phi_A) \]  

(5)

And as before, \( k \) is Boltzmann’s constant, \( T \) is temperature, \( n_i \) is the number of moles of species \( i \), \( \phi_i \) is the volume fraction of component \( i \), subscript \( m \) is maltenes, subscript \( A \) is asphaltenes. In general, for asphaltene gradients, the entropy term is not large compared to the solubility term if there is much of a GOR gradient.[22,23] The entropy term tends to randomize asphaltene distributions, thus somewhat reducing the magnitude of asphaltene gradients.

**LIVE CRUDE OIL CENTRIFUGATION**

The ideas presented herein have been tested by the first centrifugation experiments of a live black oil.[24] As shown in Fig. 5, A factor of ten gradient in asphaltene concentration was established in the centrifuge tube for an effective oil columns height of ~1000 feet.

![Figure 5. Centrifugation of a live black oil (GOR~800 scf/bbl).[24] A huge gradient of asphaltenes (10x) was obtained. Both the gravity term acting on asphaltene nanoaggregates and the solubility term (from the induced GOR gradient) combine to produce this large asphaltene gradient. The small gradient of the resins is due primarily to their lack of aggregation.](image)

**NONEQUILIBRIUM OIL COLUMNS**

Even though the discussion above for modeling asphaltene gradients has proceeded within the context of equilibrium, it is important to note that these methods readily apply to nonequilibrium columns. For example, an oil column depicted in Fig. 6 exhibits a huge GOR gradient resulting from a large ongoing charge of biogenic methane into a black oil column.[8] The lack of equilibrium is conclusively proven by noting the changing carbon isotope ratio (δC13) across the field. Biogenic methane is accumulating updip.[8] If methane with its relative large mobility is not equilibrated, then other components, especially the asphaltenes with their very low mobility are likely not equilibrated across the field.

![Figure 6. A large influx of biogenic methane into a black oil column produces a large, nonequilibrium GOR gradient. The changing CH4 isotope ratio (δC13) shows that methane is not in equilibrium.](image)

The biogenic charge into the reservoir also produced a large asphaltene gradient.[8] This gradient is described in detail elsewhere and is shown pictorially in Fig. 7.

![Figure 7. A large gradient in the asphaltene content in dead oils in a single column occurred because of an increasing nonequilibrium gas content in the oil towards the top of the column. Dissolved gas significantly reduces the ability of the live oil to dissolve asphaltenes.](image)

One might naively expect that if one starts with a black oil, adds gas, then removes the gas, that one would get back the same dead oil. Essentially, this process is what happened to the crude oils in Fig. 7; biogenic gas was added in the reservoir and all gas was flashed in the lab. Once gas is added to the black oil, the ability of the black oil to dissolve (or, more accurately, colloidal suspend) asphaltene is reduced. The greater the GOR, the less the solubility of the live crude oil for asphaltenes. The huge variation of asphaltene content in Fig. 7 reflects this fact. The eventual disposition of the redistributed asphaltenes is a function of many parameters;
possible outcomes include phase instability of the asphaltene at points in the oil column.

**DOWNHOLE FLUID ANALYSIS (DFA)**

Downhole fluid analysis (DFA) is a new technology that enables measurement of reservoir fluid gradients in a cost effective manner.[1] DFA allows matching the complexity and cost of the wireline job to the complexity of the oil column thereby enabling a greatly improved efficiency in revealing fluid and reservoir complexity.

DFA has been described in great detail in numerous papers (cf. Ref 1 and references therein). DFA measurements are performed on a wireline formation sampling and testing tool depicted in Fig. 8. DFA tools rely on optical spectroscopy measurements and also mechanical oscillator measurements for a large number of answer products. Increasingly sophisticated DFA tools have been introduced into the field over the years. Besides monitoring sample properties to determine contamination and avoid phase changes, DFA answer products include GOR, C1, C2, C3-C5, C6+, CO2, density, viscosity, relative asphaltene content and (for water) pH.

![DFA Tool with Optics Module](image)

**HEAVY END MOLECULES IN CONDENSATES.**

The modified Yen model provides the specific asphaltene structures found in crude oils as shown in case studies. The liquid column of condensate reservoirs have asphaltene-like optically colored resin compounds that are dispersed as a molecular solution.[13] Figure 9 shows a complex reservoir where two gas caps were evident in seismic.[25] The data from the Wireline formation sampling and testing tool (WFT) in the two wells depicted in Fig. 9 showed that the two gas-oil contacts differed by 20 meters TVD.

![Figure 9. A complex condensate field where two separate gas caps are thought to be connected to a common oil leg. The two gas-oil contacts differ by 20 meters TVD. Either there is a lateral disequilibrium or compartmentalization.](image)

There are two plausible, simple explanations for the differing GOCs. Either the reservoir is compartmentalized with two (presumably equilibrated) distinct fluids or the reservoir is a single compartment with a subtle lateral disequilibrium. It is known that analysis of the oil and gas column locally in each well is consistent with equilibrium (cf. Figs. 1 and 9, the discovery well).[9,25] The field development plan depends critically on which explanation is correct.

One might argue that with two separate gas caps in two local maxima, it would be almost impossible to obtain identical GOCs if any separated gas phase charged into the reservoir. That is, dissolving gas from the cap to the oil, transporting the gas laterally and finally releasing the gas from the oil to the other gas cap would take enormous time. Consequently, it is difficult to assess the connectivity issue from the light ends.

What do the heavy ends of the liquid phase of the condensate tell us? The heavy ends of the condensate liquids are asphaltene-like colored resin molecules and are expected to be molecularly dispersed in crude oil.[24] Molecules are the smallest of the three asphaltene structures shown in Fig. 3 and show little variation in the reservoir due to gravity.
However, the large condensate GOR gradient gives rise to a large variation of the solubility parameter; thus the condensate heavy ends exhibit a large variation.\[24\]

Figure 10. The DFA color variation maps the heavy ends of the condensate across the reservoir in three wells.\[25\] The continuous variation of heavy ends is consistent with an equilibrium distribution (fitted solid line) of heavy ends. The molecularly dispersed heavy ends are depicted schematically in the oil column (embedded cartoon) with increasing color due to the increasing asphaltene-like resin concentration lower in the column.

The condensate heavy ends partition entirely to the liquid phase, so the gas caps are essentially not an issue. Figure 10 shows that the heavy ends largely trend continuously across the reservoir. Moreover, the best fit line to this variation (solid curve, Fig. 10) is consistent with an equilibrium distribution of a molecular dispersion of these heavy ends.\[25\] Figure 10 shows that in two wells, the base of the column (one near the oil-water contact) have ‘too much’ color. More DFA would have been preferred to understand this higher order effect. In any event, the primary effect on the heavy end distribution is the equilibration of the heavy ends in accordance with the precepts described in the theory section herein.\[25\]

Equilibration of heavy ends in the liquid phase of a condensate reservoir requires massive fluid flow and component redistribution within the reservoir. This can only happen if the reservoir is connected. This reservoir has recently been put on line and the reservoir has indeed been proven by production to be connected.\[26\] The connectivity interpretation of the DFA data using the new heavy end theory has proven correct by production, the final arbiter.

**ASPHALTENE NANOAGGREGATES IN STABLE BLACK OIL**

In low GOR black oils that are not near their asphaltene onset pressure, the asphaltenes are largely (or entirely) dispersed as asphaltene nanoaggregates.\[10,24,27-29\] Asphaltenes especially at higher concentrations are known to self-assemble.\[13,19\] Figure 11 depicts a reservoir that most clearly proves the point.

Figure 11. One of Tahiti reservoirs showing the location of exploration and appraisal wells along with the first development well. This Tahiti reservoir contains a low GOR black oil and consists of two stacked sands that are not in pressure communication.

The Tahiti reservoir shown in Figure 11 is highly tilted and displays a large degree of vertical relief. Allochthonous salt from the Jurassic Luann salt deposit lifted part of the reservoir. The reservoir is not a rigid body, so it breaks – or faults. The biggest risk factor is whether these faults are transmissive or sealing. Can a cubic EoS be used to determine the GOR gradient to probe connectivity as the example in Fig. 1? The answer is no. The reservoir contains a low GOR black oil, thus the GOR is relatively homogenous as predicted by any cubic equation of state. Consequently, GOR and a cubic EoS cannot be used to identify possible compartmentalization or connectivity. What about the heavy ends? Figure 12 shows the DFA-measured asphaltene variation vs. height in the two stacked sands (red curve and blue curve). The DFA-measured asphaltene concentration gradient is consistent with the subsequent laboratory analysis.\[27\] The homogeneous GOR yields a negligible contribution from the solubility term. Consequently, the gravity term is responsible for the asphaltene gradient. The asphaltene particle size is consistent with laboratory determinations.
of asphaltene nanoaggregates (~2nm).[13,24] Equilibration of asphaltenes is a slow process; the asphaltenes are the least mobile component in a crude oil (especially in nanoaggregates). This asphaltene equilibrium is not consistent with flow barriers in the reservoir. Indeed, the Tahiti reservoir has been put into production and connectivity has been proven.[30]

Figure 12. The DFA-measured asphaltene content vs. depth in the Tahiti reservoir (cf. Fig. 11). The ~2.5x asphaltene concentration gradient is consistent with an equilibrium distribution of asphaltenes across the entire reservoir in the two primary sands. This indicates the reservoir is connected, [1,27] and that has been proven in production.[30] (The green curve represents a separate gradient for a small section.) The embedded cartoon shows the oil column with increasing color and nanoaggregate concentration lower in the column.

Compartmentalization is often easy to establish - similar to finding cancer. Connectivity is hard to establish – similar to establishing being cancer-free. Utilizing the combination of DFA measurements and novel asphaltene science to establish connectivity is proving to be of extreme value.

**ASPHALTENE CLUSTERS IN HEAVY OILS**

At high asphaltene concentrations, the asphaltene nanoaggregates self assemble to form clusters.[13] These large asphaltene species are greatly impacted by gravity and tend to accumulate towards the bottom of the reservoir. Consequently, even though heavy oil GORs are small yielding negligible asphaltene grading from the solubility term, the gravity term can produce huge asphaltene gradients. Figure 13 depicts such a column.

Figure 13 shows a giant asphaltene gradient of a factor of two in 60 feet. The corresponding viscosity gradient is about a factor of 30; thus this gradient is extremely important for production. The gradient in Fig. 13 is consistent with a (local) equilibrium of asphaltene clusters. The small vertical height in the column allows diffusive mixing to be far more efficient in establishing equilibrium at this single well than if across a field. We note that this heavy oil flows. If the temperature is cooled or if the asphaltene concentration increases further, then it is possible larger asphaltene structures would form, possibly producing a tar-like layer precluding flow. For the heavy oil depicted in Fig. 13, the oil flows and thus has not formed a gel. Consequently, finding asphaltene clusters in this oil is not surprising.

It is quite possible that processes acting on heavy oil columns can preclude equilibrium. For example, biodegradation can occur provided the oil column is or has previously been at a temperature of less than 80°C. The microbes live in the water and preferentially remove alkanes at the oil-water contact. A (nonequilibrium) steady state can thus be maintained by dynamic processes that are faster than (diffusive) mixing, the latter tends to drive the oil column towards equilibrium. Nevertheless, the equilibrium column gives a framework to investigate nonequilibrium columns. Moreover, it has been established that even for crude oil columns that have experienced extensive biodegradation (>6 on the Peters-Moldowan scale), these columns can equilibrate once biodegradation terminates.
for example due to increased reservoir temperature.[29]

ASPHALTENES IN UNSTABLE BLACK OILS

In stable black oils, asphaltenes are present as nanoaggregates. If the asphaltenes are destabilized, then a fraction of the asphaltenes can form clusters. Figure 14 shows such a column.

![Figure 14. Partially destabilized asphaltenes in a black oil column. The embedded cartoon illustrates the increasing asphaltene concentration towards the base of the column.](image)

Figure 14 shows a column that evidently resulted when a black oil reservoir had a late gas charge.[13] Consequently, a fraction of the asphaltenes was destabilized to form clusters thereby magnifying the effect of gravity. The GOR (~800 scf/bbl) is large enough that the column also has a GOR gradient. Consequently both the gravity and the solubility contrast give rise to a large asphaltene gradient; a factor of 10 increase in asphaltene concentration in 100 meters. The class of asphaltenes in any crude oil is chemically polydisperse; when a fraction of asphaltenes is destabilized to form clusters (partially destabilized), then other less stable fractions can undergo phase instability. The evidence supporting asphaltene destabilization by a gas charge include bitumen in the core (as shown in thin section), the crude oil being at the asphaltene onset pressure and the preferential loss of more volatile components in the crude oil. Instability of asphaltenes with gas flood in production is well known and is consistent with asphaltene instability with a gas charge (cf. Figs. 6 & 7).

Moreover, the phase unstable asphaltenes can appear as an immovable phase (tar or bitumen) in the core. The exact location of this bitumen depends on the specific parameters governing the instability. The bitumen can be formed where it is physically destabilized or it can form elsewhere and lower in the column. Previously, it had been thought that tar mats form exclusively from biodegradation. We call this an autochthonous tar mat. In addition, the physical destabilization of asphaltenes can form a separated tar mat which accumulates elsewhere in the column, we call this an allochthonous tar mat.

The appearance of tar in charge fault planes in reservoirs had previously been attributed to the initial heavy charge from kerogen. It might be possible that a tar could escape the extremely low permeability of source rock, migrate through secondary migration paths and then get stuck in large faults. It is more probable that the tar in faults is the result of physical destabilization of asphaltenes in an existing black oil with a later, light alkane charge. The dependence on reservoir properties (distance to water, temperature, charge history, etc.) of allochthonous versus autochthonous tar mats is totally different. Moreover, it is now possible to understand the asphaltene gradients and phase destabilized asphaltenes within a single formalism as described herein. Work is ongoing here to probe this issue.

CONCLUSIONS

Prior reliance of equations of state derived from the ideal gas law for crude oils precluded proper treatment of a major component of crude oils, the solid phase – the asphaltenes. The asphaltenes dramatically impact viscosity and phase behavior, thus are an important production issue. Recent advances in asphaltene science have identified three distinct species of asphaltenes that are present in crude oils; molecules, nanoaggregates and clusters of nanoaggregates. This has enabled the determination of the gravity term (among others) where size is obviously important. In addition, the solubility term is now understood to be governed in large measure by the GOR gradient which in turn depends on the magnitude of the GOR.

Asphaltene gradients can now be modeled as shown in case studies herein by extending a polymer theory previously used to treat asphaltene phase behavior. The different magnitudes of the asphaltene gradients are
shown to span a factor of 50 dependent on which species of asphaltenes is present. Consequently, the basic principles of asphaltene science are seen to account for production issues of enormous importance.

This newfound ability to treat the heavy ends in all crude oils from condensates to heavy oils has resulted from two distinct advances: asphaltene science has advanced to the point of specifying the nature of asphaltenes in crude oils, and DFA has enabled the measurement of asphaltene and GOR gradients thereby guiding general understanding and delineating specific reservoirs. The recommended work flow proven herein relies on the DFA determination of the asphaltene gradient and the GOR gradient. With this information, the asphaltene colloidal structure can be determined. Corresponding implications can then be understood such as reservoir compartmentalization and connectivity, viscosity gradients, asphaltene flow assurance concerns, bitumen in core and tar mats. Treatment of nonequilibrium gradients of asphaltenes can proceed from the foundations of the equilibrium model herein much as the cubic EoS provides a foundation for modeling nonequilibrium GOR gradients.

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[18] Professor Teh Fu Yen, University of Southern California, recently pass away. He remains an absolute giant in the field of asphaltene science and it has been a great pleasure for one of us (OCM) to have interacted with this great leader.


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