Abstract

Reservoir fluids in a single compartment can be in a state of gross thermodynamic disequilibrium. The equilibration of reservoir fluids is a slow process in part mediated via diffusion, an inherently very slow process. When reservoir fluids are subjected to other, faster processes, equilibration can be precluded. A common event in reservoirs especially in deepwater is a late gas charge into an oil-filled reservoir. In this case, the gas can quickly migrate to the top of the reservoir through fault planes without mixing with the existing reservoir fluid. This newly charge gas can then diffuse down into the oil column thereby creating very large gradients of many fluid properties such as gas-oil ratio (GOR) and bubble point pressures. In addition, asphaltene solubility is highly sensitive to GOR (as shown in the Flory-Huggins-Zuo Equation of State (FHZ EoS)), thus very large gradients of asphaltene content can likewise be established. Where solution gas is high, asphaltene instability is expected and Flow Assurance problems can occur. Gravity segregation of asphaltenes due to redistribution of the colloidal speciation of the asphaltenes in accordance with the Yen-Mullins Model can occur and results in asphaltene gravity currents. This process can result in significant variations in asphaltene concentration throughout the column. This convective process can yield large asphaltene concentrations at the base of the column thereby producing corresponding Flow Assurance concerns at the base. The combination of all these processes associated with gas charge into black oil can create a large gradient in asphaltene onset pressure (AOP). Such cases if not properly analyzed can give rise to mismanagement of Flow Assurance concerns. In this paper, we discuss case studies that exhibit such potentially problematic fluid columns. Simulated cases are also modeled to provide guidance for optimal management of AOP variations. The relationships of these Flow Assurance problems with other production problems are clarified. The ability to model asphaltene gradients with the FHZ EoS is seen to help significantly in understanding of asphaltene phase behavior of reservoir fluids.

Introduction

Reservoir fluids can undergo dynamic processes over a large span in geologic time.[1] Some Pliocene reservoirs are still actively charging and seemingly have not had sufficient time to complete their charge.[2] In these cases, thermodynamic equilibration of the fluids is simply precluded. Other, much older reservoirs, such as Lower Cretaceous, [3] or Lower Tertiary[4] have completed their charge and
have been quiescent for extended periods of geologic time. This time scale of roughly 1 million years to 250 million years represents an enormous range with respect to time needed for reservoir fluids to come to thermodynamic equilibration. Convective flows and diffusion are two processes that can migrate fluids towards equilibrium yet at very different rates. Convection, when it can occur, is a much faster process than diffusion and can occur for example if a fluid density inversion exists in the reservoir. Diffusion can always occur, yet is rather slow with diffusive times scaling as the square of distance. In many reservoir fluid processes, a combination of convection and diffusion is required to attain fluid equilibrium. In some cases, convection can redistribute fluids laterally while diffusion can redistribute fluids vertically. This results in sequential processes with fluid equilibration times that can be roughly several million years. Consequently, reservoirs (and contained fluids) that are significantly younger than several million years can exhibit fluids in gross disequilibrium [1, 2] while reservoirs and contained fluids that are significantly old than several million years can exhibit fluids in thermodynamic equilibrium. [2, 3, 4] Indeed, a reservoir that has been examined in detail contains a heavy oil rim in a large anticline with the heavy oil equilibrated throughout a ~100 kilometer rim; thus fluid equilibration can take place over enormous length scales.[3, 5, 6] This equilibration cannot be simply diffusive at this length scale as that would take ~ one trillion years or eighty time the age of the universe.

It is important to clarify the concepts of thermodynamic equilibrium of reservoir fluids because they are important to perspectives promulgated herein. Fluid equilibrium includes the requirement that a small change in externally applied conditions yields only a small change in the state of the fluid. The gravitational analogue is that a ball resting on a table is not in a stable (equilibrium) condition but is rather in a metastable condition. A small change imparted to this resting ball could cause it to roll off the table greatly changing its condition. A superheated fluid might be metastable but is not equilibrated. Another requirement of equilibrium is that there is no entropy generation and no net flux of components nor energy. Since reservoirs often have a (small) temperature difference from top to bottom, there is heat flux from higher to lower temperature. Such a heat flux is the classic definition of entropy creation. Consequently, such reservoirs are not equilibrated. However, frequently the temperature differentials and the thermal flux are quite small so the corresponding deviation from fluid equilibration can be ignored for many purposes. If the reservoir is undergoing charging then there is a mass flux and equilibrium is precluded. In a general sense, the larger the mass flux the greater the deviation from equilibrium.

In addition, crude oils are one of the most complex chemical mixtures known, and different crude oils can have remarkably different properties and compositions.[7] Indeed, even the asphaltene fraction alone is extremely complex chemical mixture.[8] Equilibrium of crude oil applies to all components of crude oils. If a particular component is out of equilibrium, then the crude oil is not equilibrated. For example, if the isotope ratio of methane carbon varies across a field, then methane is not equilibrated and thus the crude oil is not equilibrated. Charging of biogenic methane into a reservoir often leads to (monotonic) variation of the isotope ratio of methane carbon.[9, 10] Again, the extent of disequilibrium induced by such a flux is dependent on the relative size of this flux and on the reservoir fluid properties as well. Methane charging into low gasoil ratio (GOR) fluids can significantly alter GOR and saturation pressure of those localized fluids receiving the methane. Of course, the asphaltene onset pressure would also be affected. Charging of methane into a dry gas reservoir would have virtually no effect on physical properties of the reservoir fluid (except the volume of reservoir hydrocarbon would increase).

In order to determine whether a fluid is in thermodynamic equilibrium it is self-evident that a corresponding thermodynamic model is needed. In previous years, various cubic equations of state (EoS) have been the primary thermodynamic approach to treat reservoir fluids. The cubic EoS was first developed by van der Waals to treat gas-liquid equilibria. It was never designed to handle colloidal solids such as asphaltenes (that is, solids that are present in small particles that are not covalently bound). Consequently, only part of the components of crude oil had been analyzed to determine whether the reservoir fluid as equilibrated. Indeed, different components can deviate to different extents from
equilibrium depending on the impact of various dynamic fluid processes on the various components. Moreover, for low GOR oils, the equilibrium variations of GOR tend to be quite small due to the low compressibility of the corresponding oils. [11] Often, it is the asphaltenes which exhibit large gradients. Moreover for issues associated with tar mats, bitumen deposition or asphaltene Flow Assurance problems, the asphaltenes figure prominently in the concerns. For many reasons, it is desirable to analyze the state of thermodynamic equilibrium of the asphaltenes in the reservoir crude oil. Until recently, this was not possible due to the lack of fundamental chemical knowledge about the asphaltenes. Without knowing the molecular and colloidal size of asphaltenes, the effect of gravity (and other factors) cannot be predicted thereby precluding any treatment of asphaltene gradients. The nanoscience of asphaltenes has been resolved and codified in the Yen-Mullins Model.[12] This enabled development of the first predictive EoS for asphaltene gradients, the Flory-Huggins-Zuo (FHZ) EoS.[13, 14]

This new found ability to model asphaltene gradients in reservoirs has found immediate use in addressing reservoir connectivity. Essentially, if the asphaltenes are equilibrated in a field, then reservoir connectivity is likely.[15] This is because significant fluid mobility is required for the asphaltenes to equilibrate. In contrast, almost no mass transfer is required to equilibrate pressure.[15, 16] The FHZ EoS has been linked with downhole fluid analysis (DFA) because DFA is the preferred method to measure compositional gradients.[16] Figure 1 shows that the FHZ EoS can be applied to fluid types from condensate to heavy oil. In all cases, production established connectivity consistent with the DFA-measured equilibrated distribution of asphaltenes.[14] The particular asphaltene molecular or colloidal species from the Yen-Mullins Model is also depicted in Fig. 1. For the condensate, there is virtually no asphaltene, the size for the FHZ EoS is one nanometer and is consistent with heavy resin molecules. In a blue condensate, the blue color was shown to originate with perylene, a compound of approximately one nanometer in size.[17]

The FHZ EoS can also be used to model disequilibrium in crude oil columns. Figure 2 shows the well-known series of dead oil samples from a single oil column. The gradient that is seen is in asphaltene
The origin of this gradient is the following: a late gas charge entered a reservoir with a black oil. The gas quickly migrated to the top of the reservoir. The reservoir pressure was high, thus the gas dissolved in solution at the gas-oil contact (GOC). This dissolved gas then started to diffuse down the column. Where the solution gas became high, the asphaltenes were expelled (cf. Fig. 2). A theoretical treatment using the FHZ EoS plus one additional methane flux term to account this large, disequilibrium gradient proved to be successful as shown in Fig. 2. For the corresponding live oils for Fig. 2, all properties vary significantly including GOR, the saturation pressure, asphaltene content, and most likely asphaltene onset pressure. The foundation of the FHZ EoS is, of course, the Flory-Huggins theory. Many years ago, Hirschberg suggested to use the Flory-Huggins theory to account for asphaltene phase behavior and solubility. More recently, detailed studies of asphaltene phase behavior have successfully employed the Flory-Huggins theory. Figure 3 shows experimental data and theoretical modeling for the onset solubility parameter vs. n-alkane chain length. The solubility parameter \( \delta \) is key in the Flory-Huggins theory. Formally, it is defined as where \( \Delta H \) is the heat of vaporization and \( v \) is the molar volume. As the difference in solubility parameter increases between solute and solvent, the solubility goes down. This can be considered a formal representation of the well-known chemical maxim: “like dissolves like”.

Herein, we are interested in the asphaltene onset in a manner similar to Fig. 3 for an oil column that is in disequilibrium in a manner similar to Fig. 2. The Flory-Huggins-Zuo EoS is a natural way to consider this. In particular, for such a disequilibrium column shown in Fig. 2, it is desirable to understand considerations for the relative severity of Flow Assurance problems at different points in the oil column.

**FHZ and Yen-Mullins Models**

In order to treat asphaltene gradients within a proper thermodynamic formalism, it is essential to know the asphaltene particle size. Otherwise, the gravity term and other terms remain unpredictable. For many years even the asphaltene molecular weight was not known thereby precluding the ability to understand...
colloidal species. Fortunately, in recent years, the asphaltene molecular and colloidal species in crude oil and in laboratory solvents has been resolved. This solution has been codified in the Yen-Mullins Model shown in Fig. 4.[12] The Yen-Mullins model establishes that at very low concentrations heavy ends should be molecularly dispersed in crude oil; the size of the predominant molecular structure of asphaltenes is 1.5 nm (in long dimension). At higher asphaltene concentrations, such as in black oils, the asphaltene nanoaggregate of ~2 nm size dominates. This nanoaggregate consists of about six molecules. As asphaltene concentration increases further such as in mobile heavy oils, asphaltene clusters dominate. Many papers in the scientific literature have corroborated this model. For example, laser-based mass spectral measurements at Stanford University have recently confirmed that the asphaltene nanoaggregate (Fig. 4, Center) consists of about 6 molecules.[22] In addition, NMR measurements relying on both advanced spectroscopic methods and relaxation methods have confirmed the asphaltene molecular size and architecture (Fig. 4, Left) and the asphaltene cluster size (Fig. 4, Right).[23] Fluid compositional variation and the ability to utilize this asphaltene nanoscience model are important factors that can influence Flow Assurance analysis.[24, 25]

With the resolution of the size of asphaltene species in crude oil, a 1st-principles EoS for asphaltene gradients can be developed.[13, 14] A key aspect for modeling asphaltene gradients in a reservoir is the effect of gravity. The FHZ EoS extends the Flory-Huggins model, which has been successfully used to describe the solubility of asphaltenes in the maltene (the crude oil minus the asphaltene).[20, 21] Incorporating the gravity term accounts for the negative buoyancy of the asphaltene particles; this term is the Boltzmann distribution with Archimedes buoyancy in the exponential argument. The resulting FHZ EoS can thus account for asphaltene gradients in reservoir fluids. The model also accounts for solubility variations of the de-asphalted oil along the hydrocarbon column. Such variations are governed predominantly by changes in the gas-oil ratio (GOR) with height in the oil column. The various terms of the FHZ EoS and their physical meaning are described elsewhere [13, 14] and shown in Eq. 1 (below) where OD is the optical density, R is the gas constant, \( \phi \) is the volume fraction, \( v \) is molar volume, \( \delta \) is the solubility parameter, \( T \) is temperature, \( g \) is gravitation acceleration, \( p \) is density, and \( h \) is depth. The results from Eq. 1 are shown in Fig. 1 to assess reservoir connectivity.[14]

\[
\frac{OD(h_2)}{OD(h_1)} = \frac{\phi_2(h_2)}{\phi_1(h_1)} = \exp \left\{ \frac{\nu_p R (\rho - \rho_a)(h_2 - h_1)}{RT} + \frac{\nu_a R}{RT} (\delta_a - \delta) h_2^2 - (\delta_a - \delta) h_1^2 + \left[ \frac{\nu_a}{v} \right]_{h_2} - \left[ \frac{\nu_a}{v} \right]_{h_1} \right\}
\]

For low GOR crude oils, the GOR does not vary much. The reason is that these crude oils are low in compressibility. Consequently, the hydrostatic head pressure of the oil column does not increase the density at the base of the column although of course it does increase the pressure at the base. Without a density increase, in effect, the light ends are not squeezed out of the base of the column, and there is little compositional variation in the liquid phase. That is, GOR variation is small for equilibrated columns of low GOR crude oil.

The solubility parameter of Eq. 1 is strongly dependent on GOR. When there is little variation of GOR, then the solubility parameter remains largely invariant. That is, in such cases, there is little variation of
asphaltene concentration from the solubility term, the second term in Eq. 1. In addition, the entropy term is small. Consequently, the only significant term that produces asphaltene gradients in low GOR crude oils is the gravity term. The gravity term, shown in Eq. 2, and the left most term in the exponential argument of Eq. 1, depends on volume. Thus, the larger asphaltene species such as the clusters will induce a larger asphaltene gradient than the smaller species the nanoaggregate. Moreover, because the volume of the methane molecule is so tiny, the gravity induced gradients of methane are likewise very small.

The gravity term, Eq. 2, dominates for low GOR crude oils. Recently, the 100 kilometer rim of heavy oil in a giant, anticlinal reservoir was shown to fit Eq. 2 using the asphaltene cluster size.[3, 5, 6] The variation of the asphaltene concentration in this field is a factor of ten. The excellent fitting of the data over a huge gradient, over such a huge length scale proves the validity of this approach.

$$\frac{\partial \rho(h_2)}{\partial (h_2)} = \frac{\partial \rho(h_1)}{\partial (h_1)} \exp \left\{ \frac{\varphi_0(\rho - \rho_0)(h_2 - h_1)}{RT} \right\}$$

\[2\]

### Gas Charge into a Black Oil Reservoir

Gas frequently charges into reservoirs. Fig. 5 shows seismic images of a large gas chimney.[26]

Gas addition to black oil destabilizes the asphaltenes. If the gas addition is relatively slow, the asphaltenes can migrate to the base of the oil column in the form of asphaltene clusters.[3, 5, 6] In this case there is an increase in asphaltenes at the base of the column. If the increased concentration of asphaltenes exceeds the solvency capacity of the crude oil, then a tar mat can form. Continued gas charging then provides a mechanism to create very thick tar mats.[3, 5, 6] If the gas addition is rapid, there can be upstructure bitumen deposition.[2] In such cases, there should not be much of an increase in asphaltene at the base of the oil column. Of course, there could be intermediate cases with deposition both upstructure and at the base. Flow Assurance issues depend on the particular scenario that has taken place.

We are interested in assessing Flow Assurance related issues with the oil column depicted in Fig. 2. The corresponding PVT data for that column is shown in Fig. 6.[18] The large change in saturation pressure and GOR at the top of the column is due to gas diffusion into the oil. That is, the gas from the late charge migrates to the top of the oil column without mixing with existing reservoir hydrocarbons.[27] The gas can then diffuse down into the oil column increasing GOR, saturation pressure and decreasing asphaltene content. In this column there is a sharp increase in %-asphaltene at the base of the column. This is consistent with a migration of the destabilized asphaltenes to the base of the oil column. The corresponding PVT data is shown in Fig. 6. The lower left plot in Fig. 6 shows the large gradient at the base of the column presuming asphaltene clusters of 5.4nm and use of just the gravity term, Eq. 2. There is little variation of the GOR at the base of the column, thus use of Eq. 2 is reasonable. The slightly larger cluster size (5.4nm) rather than 5.0nm per Fig. 2 is likely due to 1) some disequilibrium and 2) some GOR gradient at the base of the column which can increase the asphaltene gradient. Accounting for this
solubility terem effect would decrease the gravity effect somewhat thus reducing the estimated cluster size closer to 5.0 nm.

A question remains why the asphaltene cluster gravity plot accounts for the asphaltene data so well. There are two important considerations. First, asphaltene clusters never persist at low concentrations of asphaltenes in an equilibrium setting. Instead, asphaltene clusters are found at the base of the column with asphaltene nanoaggregates above the clusters. Asphaltene nanoaggregates have a much smaller size and thus produce a much small asphaltene gradient.[3, 5, 6] Thus, the asphaltene cluster gradient cannot account for the tiny asphaltene concentration at the top of this column. This low asphaltene content is accounted for by the very large solution gas content at the top of the column. That is, it is solvency (or the lack thereof) not gravity that accounts for the tiny asphaltene fraction at the top of the column. In other words, the excellent fit of the single gravity term to all the asphaltene data in the column is fortuitous. The fit of Eq. 2 to the measured asphaltene gradient is meaningful for only the lowest 100 feet in the column. Second, Eq. 2 presumes equilibrium. Yet the GOR at the top of this column is grossly out of equilibrium. The question remains why the asphaltene gradient at the base of the column appears not far from equilibration while the GOR at the top of the column is grossly out of equilibrium. The working hypothesis is that the rate of asphaltene addition to the bottom of the column depends on gas diffusion.

Figure 6—PVT data for the oil column depicted in Fig. 2.[18] The high and variable GOR and saturation pressure curves toward the top of the column are due to gas diffusion into the oil column from above. The large and variable asphaltene concentration at the bottom of the column is plausibly due to destabilized asphaltenes migrating to the base of the oil column in the form of clusters. The lower right plot shows lab data and the fit with Eq 2 using clusters of 5.4 nm. The excellent fit is meaningful for the lowest 100 feet in the column. The excellent fit towards the top of the column is fortuitous (see text).
down the column and setting up a density inversion via diffusion and on the asphaltene gravity current (advective flow). This net process is rather slow. Consequently, some asphaltene equilibration in the bottom 50 feet to 100 feet vertical can be attained via a combination of advective flow and diffusion.

**Flow Assurance Considerations**

In this case, whether or not asphaltenes are likely to phase separate from the oil at specific heights in the oil column, the situation is identified as the Flow Assurance propensity. The Flow Assurance propensity can vary from top to bottom of the oil column. We consider a “typical oil column” where gas has charged into black oil leaving very large fluids gradient. For such a disequilibrium condition, the fluid properties such as saturation pressure, compressibility are expected to vary throughout the column. Moreover, there is no expectation that this variation must be monotonic. There could be a maximum potential for Flow Assurance problems with asphaltenes at an intermediate location in the column. For the following analysis we are not trying to treat the oil column depicted in Fig. 2. Instead, we are using this oil column as a guide to understand asphaltene Flow Assurance concerns in similar situations.

Reservoir crude oils that are particularly sensitive to undergo asphaltene destabilization with pressure reduction are highly undersaturated, compressible crude oils, the de Boer conditions. [28] If a crude oil is saturated, then a reduction of pressure will cause gas liberation thereby increasing the solvency of the crude oil for asphaltenes. If a crude oil is incompressible, then a drop in pressure does not alter the crude oil in any way (above the saturation pressure). Crude oil compressibility is directly related to the content of solution gas. Higher GOR oils are compressible, low GOR crude oils are relatively incompressible. Finally, if a crude oil has vanishing amounts of asphaltene, it will be less likely to give asphaltene Flow Assurance problems if all other factors are equal.

**Figure 7**—A) Saturation pressure and formation pressure vs. depth for a column undergoing active gas charge (cf. Fig. 2). B) Compressibility of this same oil column.

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**Figure 7A**, plots the saturation pressure and formation pressure as a function of depth for a column with disequilibrium gas addition at the top. The largest undersaturation of the oil is at the base of the column, indicating Flow Assurance problems predicted from this factor increase with depth. **Fig. 7B** plots the compressibility of this same crude oil. The compressibility is highest at the top of the column indicating Flow Assurance problems predicted from this factor decrease with depth.

**Figure 8A** plots the crude oil density as a function of height. The impact density has on asphaltene disposition is primarily through the solubility parameter. **Fig. 8B** plots the solubility parameter as a function of height. The solubility parameter increases with depth thus from this parameter the asphaltenes become more stable with depth.
The factors that influence variation of asphaltene Flow Assurance susceptibility with height are 1) the pressure differential between saturation and formation (increasing problems with depth), 2) compressibility (decreasing problems with depth), 3) solubility parameter (decreasing problems with depth) and 4) asphaltene content (increasing problems with depth). The overall sensitivity to asphaltene Flow Assurance problems with depth depends very much on the relative importance of these opposite trending parameters. For example, for a case where the pressure differential goes to zero at the top (e.g. when a gas cap is present), then any reduction in pressure causes gas to evolve thereby stabilizing the asphaltenes. In such a case, the asphaltene deposition problems will be lower in the column below the gas-oil contact (GOC).

In contrast, when all oils in the column are highly undersaturated, then the maximum compressibility could dominate yielding the biggest asphaltene problem at the top of the column.

Figure 9 shows the reduction of the oil solubility parameter as a function of added gas to a black oil. In the array of bottles in Fig. 2, the gas content is particularly high at the top of the column. Indeed, much of the asphaltene has already been expelled from this oil as seen by the light coloration towards the top of the column as well as the asphaltene content displayed in Fig. 6. The little asphaltene that remains in the oil at the top is unstable and can flocculate with a pressure drop. As shown in Fig. 6, the saturation pressure is high for the disequilibrium column in Fig. 2. If the reservoir pressure is close to the saturation pressure at the top of the column, then a pressure reduction will cause this oil to evolve a gas phase. Just as added gas destabilizes asphaltenes, the loss of gas stabilizes asphaltene. Consequently for this reservoir pressure, the oil in this column that is more susceptible to asphaltene flocculation is not at the very top but part way down the column where the saturation pressure is lower, so a larger pressure drop can occur without evolving a gas phase. For high reservoir pressure, a large pressure drop will not result in gas
evolution. In this case, the oil at the top can undergo a large pressure drop, is compressible, and has unstable asphaltene. Thus, the instability from high solution gas can shift towards the top of the column.

A second mechanism can yield asphaltene instability. The gas addition can result in asphaltene being ‘pumped’ to the base of the oil column upon an increase of solution gas at the crest.\cite{3, 5, 6} The corresponding mechanism is described in the next section. As asphaltene is added to the (black) oil at the base of the column the concentration rises until it gets close to and even exceeds the solvency capacity of the oil for asphaltenes. If the concentration exceeds this solvency capacity, then a tar mat can form.\cite{3, 5, 6} For crude oils close to this instability concentration, asphaltene flocculation could occur with a pressure reduction. Fig. 10 shows solubility parameter of deasphaltene oil as a function of asphaltene onset concentration in vol%.

Instability for asphaltenes can be caused by reducing the solvency of the liquid phase for asphaltenes by adding gas, Fig. 9, or by adding asphaltene to a fixed liquid phase, Fig. 10. The gas addition happens first at the top of the column while the added asphaltene happens at the base of the column. Because the high asphaltene concentrations correspond to asphaltene clusters, the corresponding asphaltene gradients are large. Thus, the highest asphaltene concentrations span a limited vertical extent at the base of the column thus limiting corresponding Flow Assurance concerns to the same limited vertical extent. Pressure reduction can cause these unstable asphaltenes to flocculate. Thus, Flow Assurance problems can occur both at high points in the column (from solution gas destabilization) and at the base of the column (from asphaltene addition from above).

**Gravity Driven Migration in Inclined Porous Layers**

Reservoir fluid equilibration and asphaltene content distribution are established mainly by diffusion and convection through geological time. Diffusion alone is an extremely slow process which can take up to $10^{12}$ (one trillion) years to equilibrate a very large reservoir. Convection on the other hand, as will be shown, propagates orders of magnitude faster as long as there is a fluid density inversion to drive this process. When asphaltenes destabilize at the crest of the reservoir due to processes such as late gas charge, the asphaltenes can form clusters,\cite{6} the largest of the stable colloidal particles of asphaltenes.\cite{12} These clusters can then migrate both via diffusion and convection to set up large asphaltene gradients vertically.
over the height of the formation. The convective component of flow is due in part to displacement associated with new fluid entry into the reservoir. Some of these considerations of asphaltene instability apply for gas injection in EOR, however, that process is very rapid, consequently the asphaltene deposition is local in the gas-oil transition zone.[29] In any event, with asphaltene cluster formation and accumulation at the base of the transition zone, the crude oil at the base of the crest can be higher density than the crude oil in the flank. Fig. 11 shows a schematic of this circumstance. This density inversion can drive convection (or more accurately advection if one considers the suspended nanocolloidal asphaltene as a separate phase). With a sufficiently large density inversion, asphaltenes can migrate in the form of gravity currents to the base of the oil column.

Gravity currents are of interest in many natural and industrial applications, notably injection and storage of CO₂.[30–33] In some cases gravity currents also play a critical role in the migration of asphaltenes.[30] In this section we outline a few numerical results associated with the behavior of gravity currents in order to provide insight on the mechanism of asphaltene migration.

We consider the problem of an inclined planar porous and permeable layer initially saturated with oil with lower density. Following the asphaltene instability discussed above, a density inversion of is created relative to the crude oil below, yielding gravitational flow (cf. Fig. 12). The volume of the current initially increases in time due to continuous gas charge, hence we approximate the volume with the form volume = q \cdot t^\alpha, \; 0 < \alpha < 1, where q is the flux coefficient. α=0 corresponds to instant release of fixed volume; α=1 corresponds to constant flux release; and 0 < α < 1 describes increasing volume with slowly decaying influx through time.

Combining Darcy’s law and the conservation of mass, the above problem satisfies the convection-diffusion equation below.[31, 33]

\[
\frac{\partial h}{\partial t} = \frac{\Delta \rho g k}{\phi \mu} \left( -\sin \theta \frac{\partial h}{\partial x} + \frac{\cos \theta}{2} \frac{\partial^2 h}{\partial x^2} \right)
\]

where x is the distance from the initial influx location, h is the height at given location, k is permeability of the layer and \( \phi \) is porosity, \( \mu \) is the viscosity of both fluids, and \( \theta \) is the dip angle of the slope. The
The first term on the right hand side represents the gravity driven convection downslope, and the second term represents spreading perpendicular to the slope.

Applying numerical techniques such as scaling and similarity solution to the above equation, it can be shown that the initial downslope extent varies slowly at time magnitude of $t(a/\mu)^{1/4}(t/\mu)^{1/2}$. After sufficient time, the current reaches a second regime, where downslope flow dominates the propagation at the constant characteristic velocity given in Eq. 4.

\[ v_c = \frac{\Delta \rho g k \sin \theta}{\phi \mu} \]

In this regime, the downslope location increases linearly with time, and does not depend on the assumption of the volume of the gravity current.

In Fig. 13, we plot the variation of the characteristic velocity under different combinations of reservoir parameters. Fixed parameters are $k = 300 \text{mD}, \phi=0.2$, and asphaltene cluster radius $r = 2.5 \text{nm}$. For comparison, we also plot the diffusion velocity computed by the Stokes-Einstein equation. The study clearly shows the different propagation scale between diffusion and convection of the asphaltenes: at $\mu = 1 \text{cP}, \theta = 5^\circ, = 0.1\%$, the average diffusion speed is 100m per million years (MYs), while the gravity current velocity is 32km/MYs. With this speed the gravity current can drive the asphaltenes all the way to the base of the oil column rapidly in geologic time (but not in production time). Importantly, the equations show that the diffusion length scale varies with $t^{1/2}$, while the convection length scale is linear to $t$.

The result quantitatively reveals that the time frame required for fluid equilibration is on the order of million years, although sensitively depending on the amount of density inversion $\Delta \rho$ and dip angle. Crude oils are truly Newtonian so no barrier to flow exists once any density inversion is formed. However, with vanishing density inversions, the gravity current velocities are likewise vanishing. Consequently, with very small density inversions, the asphaltene accumulation tends to remain in the vicinity where it initially forms, until sufficient density inversion is evolves. Also, the velocity may vary dramatically with viscosity. As the asphaltenes accumulate, viscosity increases exponential with the asphaltene concentra-
tion. When the viscosity reaches a very high value, e.g. 1000 cP, both the gravity current and diffusion process may cease to propagate. These very high concentrations and viscosities apply at the base of the column.

Conclusions
Optimal production of reservoirs requires accurate analyses and mitigation of Flow Assurance concerns. Fluid compositional variation in reservoirs is now widely acknowledged. In addition, these variations can be in disequilibrium. The advent of the Flory-Huggins-Zuo EoS with its reliance on the Yen-Mullins Model of asphaltene nanoscience enables thermodynamic analysis of asphaltene gradients. Consideration is given herein as to the impact of disequilibrium distributions of asphaltenes on Flow Assurance susceptibility for crude oils throughout reservoirs. In some disequilibrium cases, the most sensitive oils are towards the middle of the oil column, in other cases instability can happen at the top and/or the base of the oil column. The instability at the base of the column is due in part to asphaltene gravity currents which are indentified herein to be linked to asphaltene “clusters” of the Yen-Mullins Model. This instability can also produce regional tar mats that seal off the aquifer. Methods utilized in this analysis can be applied generally in reservoirs to help guide sample acquisition and analysis of Flow Assurance. These methods herein become more robust if the reservoir is understood within a perspective of a petroleum system especially when coupled with asphaltene thermodynamics and fluid mechanics. Indeed, such a broad perspective is useful for many concerns of production optimization; unsurprisingly, Flow Assurance falls within this category.

NOMENCLATURE

AOP - asphaltene onset pressure
EoS - equation of States
FHZ - Flory-Huggins-Zuo
GOR - gas-oil-ratio
\( H \) - enthalpy, J
OD(h2) - optical density at depth 2
OD(h1) - optical density at depth 1
R - universal gas constant, MPa-m³/mol-K
T - temperature, K
TVD - true vertical depth, m or ft
\( g \) - acceleration, 9.81 m/s²
\( h \) - the height at given location, m
\( h2 \) - depth 2, m
\( h1 \) - depth 1, m
k - permeability, D or m²
q - the flux coefficient
r - asphaltene cluster radius, nm
t - gas charge time, s
x - the distance from the initial influx location, m

Greek Letters

\( \alpha \) - index of gas charge time, 0< \( \alpha \) <1
\( \Delta \) - difference
\( \delta_a \) - solubility parameter of asphaltene, MPa¹/²
\( \delta \) - solubility parameter of bulk fluid
\( \theta \) - the dip angle of the slope, °
\( \mu \) - fluid viscosity, cP
\( \nu_a \) - molar volume of asphaltene, cm³/mol
\( \nu \) - molar volume of bulk fluid, cm³/mol
\( \nu_c \) - the characteristic velocity, m/MYr
\( \rho_a \) - asphaltene density, kg/m³
\( \rho \) - density of bulk fluid, kg/m³
\( \varphi \) - porosity
\( \varphi_a(h_2) \) - volume fraction of asphaltene at depth 2
\( \varphi_a(h_1) \) - volume fraction of asphaltene at depth 1

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