

# Modeling of Asphaltene Grading in Oil Reservoirs

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## ABSTRACT

Reservoir fluids frequently reveal complex phase behaviors in hydrocarbon columns owing to the effects of gravity, thermal diffusion, biodegradation, active charging, water washing, seals leaking, and so on. In addition, the formation compartmentalization often causing discontinuous distributions of fluid compositions and properties makes the proper fluid characterization and reservoir architecture even more challenging yet compelled. The recognition of compositional grading and flow barriers becomes a key to accurate formation evaluation in a cost effective manner. Downhole fluid analysis (DFA) of asphaltene gradients provides an excellent method to delineate the complexity of black oil columns. In this paper, a methodology was developed to estimate downhole asphaltene variations with depths using an equation-of-state (EOS) approach coupled with DFA measurements. DFA tools were used to determine fluid compositions of CO<sub>2</sub>, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>-C<sub>5</sub>, C<sub>6+</sub>, gas-oil ratio (GOR), density and the coloration (optical density) associated with asphaltene contents at downhole conditions. The delumping and characterization procedures proposed by Zuo et al. (2008) were employed to obtain the detailed compositions excluding asphaltenes. In addition, a molar mass distribution of asphaltenes was described by a three-parameter Gamma probability function. The Gaussian quadrature method was used to generate asphaltene pseudocomponents. Five pseudocomponents were employed to represent the normal asphaltene nanoaggregates. Asphaltene distributions in oil columns were computed by tuning the molar mass of asphaltene nanoaggregates against the DFA coloration logs at a reference depth. The methodology was successfully applied to investigate black oil reservoir connectivity (or flow barriers) for offshore field cases. The analysis results were consistent with the subsequent production data and analytical chemistry. Furthermore, for simplicity, it is reasonable to assume that asphaltenes have average properties such as molar mass in entire oil columns. The results obtained in this work demonstrate that the proposed method provides a useful tool to reduce the uncertainties related to reservoir compartmentalization and to optimize the DFA logging during acquisition.

**Keywords:** Reservoir Connectivity, Asphaltene Gradients, Equations of State, Downhole Fluid Analysis

## 1. Introduction

In the past few decades, fluid homogeneity has often been assumed in a reservoir. Reservoir fluids frequently reveal complex phase behaviors in single oil columns owing to gravity, thermal gradients, biodegradation, active charging, water washing, seals leaking, and so on. In addition, reservoir compartmentalization often leads to discontinuous compositional distributions at least of one fluid analyte, which is the biggest risk factor in deepwater oil production. A density inversion (higher density fluids are in the shallower oil column) usually implies a likely sealing barrier. Knowing actual fluid profiles in the reservoir enables identification of corresponding compartments. Consequently, the family of DFA measure-

ments is expanding in part to enable greater efficacy in reservoir characterization. Consequently, identifying continuous fluid gradients in the reservoir provides a method to suggest connectivity of the reservoir. In particular, since continuous gradients are generally produced by time dependent mechanisms, the existence of fluid gradients implies connectivity albeit with an unknown time scale. Nevertheless, if considerable fluid flow is required to yield such a gradient, this suggestion of connectivity is much more powerful than that of pressure communication where little fluid flow is required. In particular, if the asphaltenes are observed to have been equilibrated across a reservoir, laterally and vertically, this is a strong connectivity because 1) asphaltenes necessarily charge into the reservoir in a much nonequilibrated state and 2) to

equilibrate the component of crude oil with by far the least mobility necessitates substantial permeability. We note that measurements of fluid gradients are a far better way to detect connectivity than measurement of homogeneous properties of a fluid. One could easily imagine a single reservoir charged with a homogeneous fluid, where the reservoir subsequently develops a sealing barrier either from compaction or faulting. Maintaining continuous gradients in evolving separate compartments is much harder to justify. DFA has been used to measure continuous fluid profiles and stair-step discontinuous fluid properties addressing reservoir connectivity and compartmentalization. Fluid compositional variations are very useful to identify sealing barriers or compartments in hydrocarbon columns [1,2].

Downhole fluid analysis (DFA) measurements provide a useful tool to determine the insitu compositional gradients in real time. Recently, Zuo *et al.* [3] integrated the equation of state (EOS)-based DFA log predictions with DFA measurements to delineate the complexity of reservoir fluids and reservoir architecture. This methodology is the most suitable for the reservoirs that exhibit significant compositional grading of at least one chemical analyte. As mentioned by Hoier and Whitson [4] and Mullins [5], for equilibrium fluid distributions, the variations of fluid compositions and properties are usually small with depth if the reservoir conditions are far away from the critical point and the saturation point (e.g. highly undersaturated black oil). This especially applies to the alkane distributions [5]. For example, a case study showed that in an undersaturated black oil reservoir, the gas-oil ratio (GOR) and compositional gradients were small for large sand bodies in Gulf of Mexico (GoM) [1,2]. Nevertheless, the asphaltene gradient was rather substantial considering the 1000 meters vertical offset of the tilted sheet reservoir. The flow connectivity in the reservoir might not be identified according to the information of bulk fluids such as compositions, GOR and density. Fortunately, the DFA tools not only measure bulk fluid properties like compositions of  $C_1$ ,  $C_2$ ,  $C_3$ - $C_5$ ,  $C_{6+}$  and  $CO_2$ , GOR and density but also coloration which is associated with asphaltene contents.

Asphaltenes are defined by a solubility classification, for example, soluble in toluene, insoluble in n-heptane. The asphaltenes are the heaviest components of crude oils with the least diffusivity and have the greatest grading with depth due to a gravitational force. In the cases shown by Mullins *et al.* [1], Betancourt *et al.* [2] and Indo *et al.* [6], the detailed DFA and laboratory analyses of asphaltene contents indicated the evident asphaltene gradient with depth while the resin gradients are much smaller than asphaltenes. The asphaltenes are dispersed in crude oils as nanoaggregates. This information pro-

vides us a new powerful method of determining flow connectivity (barriers) in the reservoir by measuring asphaltene (coloration) contents with depth at downhole conditions, especially when bulk fluid property and compositional gradients are not observable.

Continuous and equilibrium asphaltene gradients have been observed in deepwater oil fields [1,2,7]. In order to establish the asphaltene gradient that is in equilibrium, it is required to establish the colloidal nature of asphaltenes in crude oil [1]. It has been established that asphaltenes are nanocolloidally dispersed in a laboratory setting as well as a field setting. We note that higher aggregation (a cluster of nanoaggregates) exists in the reservoir for either large asphaltene mass fractions such as heavy oils and/or unstable crude oils, but there is a class of black oils with asphaltenes dispersed as  $\sim 2$ nm nanoaggregates. With this knowledge equilibrium distributions of asphaltenes across a field can be established. Asphaltenes in reservoir crude oils, dispersed as asphaltene nanoaggregates, have by far the lowest rate of diffusion compared to any crude oil components. Consequently, when they are in equilibrium throughout a column, then massive fluid flow is indicated thereby positively constraining connectivity. Nevertheless, the time frame is still unknown in these novel analyses. Still the constraint indicates greater connectivity than simply pressure communication which requires almost no fluid flow at geological time scales.

Current DFA tools can measure the coloration of reservoir fluids which is associated with the asphaltene contents. Mullins *et al.* [1] developed a method to calculate asphaltene gradient combining DFA data with the Boltzmann gravitational equation. However, as mentioned by Hirschberg [8], the Boltzmann equation is valid only for ideal solutions. The non-ideality should be taken into account by either the activity coefficient model like a Flory-Huggins type solubility model or the EOS.

Up to now, no one has applied EOS approach to describe an asphaltene gradient in reservoirs although there have been a lot of publications on modeling asphaltene precipitation (onset) using EOS approach in the open literature except for work in the references [9]. Following the traditional EOS approach which has been broadly used for modeling reservoir fluids, Nghiem *et al.* [10,11] arbitrarily split the heaviest component ( $C_{31+}$  fraction) in the crude oil into two parts: non-precipitating and precipitating components. The precipitating component was considered to be an asphaltene component. Qin *et al.* [12] implemented the model of Nghiem in their compositional model. They treated asphaltenes as a pure component with the same critical properties as heavy hydrocarbons, except for the binary interaction parameters. Pedersen and Christensen [13] treated the aromatic fraction of  $C_{50+}$

as asphaltenes. The authors mentioned above assumed that asphaltenes are monomers and part of  $C_{n+}$  fraction (e.g,  $C_{31+}$ ,  $C_{36+}$ ) in crude oils, which is contradicted with the recent observations in advanced asphaltene science that asphaltenes are dispersed as nanoaggregates in crude oils [1,2,6]. Most recently, the EOS approach was employed to account for the nonideality of oils [9] and a methodology for interpreting downhole fluid analysis was developed for estimating downhole asphaltene variations with depth. The methodology can be integrated into the new workflow [3,9,14] as one useful analysis means in analyzing asphaltene coloration gradients. However, the EOS approach developed by Zuo *et al.* [9] treated asphaltenes to be a single pseudocomponent which is too simple because asphaltenes are defined as the crude oil components soluble in toluene but insoluble in n-alkanes such as n-heptane. The asphaltenes are mixtures which have components in a wide range of molar masses. Therefore, distribution functions and proper characterization of asphaltenes are highly demanding to describe asphaltene components in the EOS approach.

In this work, the EOS approach was employed to account for asphaltene gradients in reservoirs. A three-parameter Gamma distribution function was used to describe asphaltenes. Two field case studies were presented. The results in both case studies were proved by the subsequent production data and analytical chemistry. The results show that the developed methodology can be integrated into the new workflow [14] as one useful means in analyzing asphaltene coloration gradients and in discerning reservoir connectivity.

## 2. Asphaltene Molar Distributions and Asphaltene Characterization

Recently, Pomerantz *et al.* [15] determined molar mass distributions of asphaltene monomers using two-step laser mass spectrometry. The results show that petroleum asphaltenes without aggregation have a peak at every nominal mass under an envelope beginning at 200 g/mol, peaking at ~600 g/mol and extending to 1000~1500 g/mol. Mullins *et al.* [16] reviewed the open literature on asphaltene molar mass measured by different methods and concluded that petroleum asphaltenes have a number average molar mass of ~750 g/mol ( $\pm 200$  g/mol) with a range of 500–1,000 g/mol. As mentioned by Mullins in his new book [17] and the references [1,2], asphaltenes are dispersed in crude oil as nanoaggregates with 4~10 monomers and ~2 nm in diameter. Hence, the molar masses of asphaltenes in black oil are in a range of 500–7,500 g/mol from molecules to nanoaggregates (precluding clusters). On the other hand, asphaltenes may differ at different depths because asphaltenes are defined as a solubility class. Therefore, distribution functions are

required in characterizing asphaltene components in the EOS approach because a single component may not be good enough for asphaltenes.

The three-parameter Gamma function is chosen for describing molar mass distribution of asphaltene nanoaggregates [18-20]. The probability density function,  $p(x)$ , is given by

$$p(x) = \frac{(x - M_{\min})^{\alpha-1} \exp[-(x - M_{\min})/\beta]}{\beta^\alpha \Gamma(\alpha)} \quad (1)$$

where  $\alpha$ ,  $\beta$  and  $M_{\min}$  are the three parameters defining the distribution.  $M_{\min}$  can be set to the average molar mass of asphaltene monomers [16] for asphaltene nanoaggregates since it represents the minimum molar mass to be included in asphaltene nanoaggregates (e.g., 500 g/mol). If  $\alpha$  is given,  $\beta$  can be estimated by

$$\beta = \frac{(M_{\text{avg}} - M_{\min})}{\alpha} \quad (2)$$

The parameter  $\alpha$  can be determined by fitting experimental data of asphaltene distributions. For most asphaltenes and bitumens,  $\alpha = 3.5$  is suitable [21]. Therefore, the average molar mass of asphaltene nanoaggregates is only one adjustable parameter in the distribution function, which can be determined by matching the DFA color gradient data in oil columns. The average molar mass of asphaltene nanoaggregates is adjusted to match DFA color gradient data (typically,  $M_{\text{avg}} = \sim 2,000$  g/mol) with ~2 nm in an average diameter.

The Gaussian quadrature method is used to discretize the continuous Gamma distribution using  $N$  quadrature points [19]. Number of pseudo-components ( $N$ ) can be from one to 30 for representing asphaltenes (typically 5).

The asphaltene molar mass distribution function can be incorporated into the generalized asphaltene gradient formula described below using the equation of state (EOS).

## 3. Generalized Formula for Compositional and Asphaltene Grading with Depth

Compositional grading in reservoir columns has been studied by many researchers [3,4,22,23] since 1980s. For a mixture of reservoir fluids with  $N$ -components, a set of mass flux equations for all components are expressed as

$$J_i = J_i^{\text{Chem}} + J_i^{\text{Grav}} + J_i^{\text{Therm}} + J_i^{\text{Pres}} \quad i = 1, 2, \dots, N, \quad (3)$$

where  $J_i$  is the mass flux of component  $i$ . The superscripts *Chem*, *Grav*, *Therm* and *Pres* stand for the fluxes owing to chemical, gravitational, thermal and pressure forces, respectively.

To calculate compositional gradients with depth in a hydrocarbon reservoir, it is usually assumed that all the

components of the reservoir fluids have zero mass flux, which is a stationary state in absence of convection [4]. At the stationary state, the fluxes in Equation (3) are equal to the external flux at the boundary of the system. The external flux could be an active charge [22],  $J_i^e$ . It is assumed that the external mass flux is constant over the characteristic time scale of filing mechanisms in the formation.

By taking into account the driving forces due to chemical, gravitational, pressure, thermal impacts and the external flux, the resulting equations are given by

$$\sum_{j=1}^N \left( \frac{\partial \mu_i}{\partial n_j} \right)_{T,P,n_{j \neq i}} \nabla n_j - (M_i - \bar{v}_i \rho) g + \frac{F_{Ti}}{T} \nabla T + \frac{J_i^e RT}{x_i \rho D_i} = 0, \quad (4)$$

$$i = 1, 2, \dots, N$$

where  $\mu_i$ ,  $x_i$ ,  $v_i$ ,  $M_i$ ,  $D_i$ ,  $g$ ,  $R$ ,  $\rho$  and  $T$  are the chemical potential, the mole fraction, the partial molar volume, the molar mass and diffusion coefficient of component  $i$ , the gravitational acceleration, universal gas constant, the density, and the temperature, respectively.  $F_{Ti}$  is the thermal diffusion flux of component  $i$  and  $n_j$  is the mole number of component  $j$ .

The thermal diffusion flux of component  $i$  ( $F_{Ti}$ ) can be calculated by the different thermal diffusion models. An example is the Haase expression [23]

$$F_{Ti} = M_i \left( \frac{H_m}{M_m} - \frac{H_i}{M_i} \right) \quad (5)$$

where subscripts  $m$  and  $i$  stand for the property of the mixture and component  $i$ , respectively.  $H$  is the molar enthalpy. Pedersen and Lindeloff [23] developed expressions for calculating enthalpy. However, the values of ideal gas enthalpy for  $C_3$  and  $n-C_4$  are determined by optimizing absolute ideal gas enthalpy at 273.15 K and that for  $C_1$  was arbitrarily set to zero. The  $H$  values can be treated as adjustable parameters for pseudo-components to match DFA data in this work. The chemical potential is calculated through the calculation of fugacity. The resulting equations are given by

$$\Delta(\ln f_i) - \frac{M_i g \Delta h}{RT} + M_i \left( \frac{H_m}{M_m} - \frac{H_i}{M_i} \right) \frac{\Delta T}{T} + \frac{J_i^e}{x_i \rho D_i} = 0, \quad (6)$$

$$i = 1, 2, \dots, N$$

where  $f_i$  is the fugacity of component  $i$  and  $h$  stands for the vertical depth. An EOS can be used to estimate the fugacity of component  $i$ .

The critical properties, acentric factors of components are required for the EOS to calculate fugacity coefficients. The delumping and characterization procedures of

Zuo and Zhang [24] and Zuo *et al.* [25] are applied to characterize single carbon number and plus fractions of reservoir fluids at a reference depth. The asphaltene components are characterized by the method described in the previous section. The EOS is used to estimate fugacity. The DFA and/or PVT data are matched by tuning the EOS parameters to establish a reliable fluid EOS model. The compositions at depth  $h$  are obtained by solving Equation (6) numerically based on the data at the reference depth.

In the reference [9], the EOS was used to estimate asphaltene grading (profiling) in oil columns. However, asphaltenes are simply treated to be a single pseudocomponent. It is known that asphaltenes are a mixture whose molar masses vary over a wide range. Therefore, the asphaltene molar mass distribution function mentioned previously is introduced into the EOS approach. By doing this, everything is kept the same as described in the reference [9] but asphaltenes are treated as multiple pseudocomponents using the molar mass distribution function documented in the previous section to obtain mole fractions and molar masses.

The properties of the asphaltene pseudocomponents such as their critical temperatures ( $T_c$ ) in K, critical pressures ( $P_c$ ) in atm and acentric factors ( $\omega$ ) are computed by the correlations in terms of asphaltene molar masses. It is assumed that asphaltene properties follow the same trend as the pseudocomponents. The correlations were then obtained by fitting the pseudocomponent data characterized by the procedures of Zuo and Zhang [24] and Zuo *et al.* [25] for more than 10 different crude oils. The correlation are given by

$$P_{ci} = 53.6746 M_i^{-0.2749} \quad (7)$$

$$T_{ci} = 173.3101 \ln M_i - 439.9450 \quad (8)$$

$$\omega_i = 0.343048 \ln M_i - 1.26763 \quad (9)$$

The density of asphaltene pseudocomponents in  $\text{kg/m}^3$  can be calculated by the expression from [26,27]

$$\rho_i = 670 M_i^{0.0639} \quad (10)$$

where  $M_i$  is the molar mass of asphaltene pseudocomponent  $i$ . We can also set it as a fixed value of  $1200 \text{ kg/m}^3$  for all asphaltene pseudocomponents as done by Mullins [1] and Wang and Buckley [28].

The asphaltene properties are dependent on molar mass and density just like typical hydrocarbon pseudocomponents. The volume translation parameter is estimated by matching the specific gravity of asphaltene components at standard conditions.

## 4. Results and Discussions

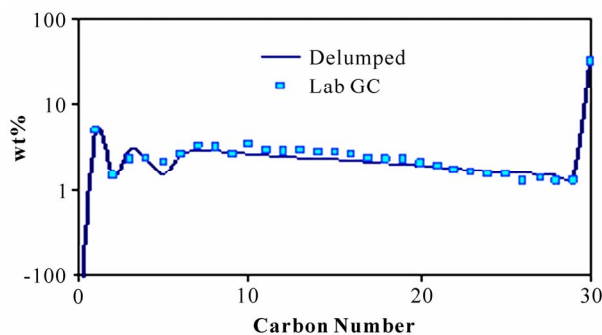
### Case 1

The Tahiti field was studied by Betancourt *et al.* [2] and

Mullins *et al.* [1] using the Boltzmann distribution equation. The reservoir has a 1,000-m vertical column of highly undersaturated black oil with GOR in a range of 90 to 116 m<sup>3</sup>/m<sup>3</sup>, which slightly decreases with depth. The formation has two main sands: M21A and M21B, but are not in pressure communication, so are not in flow communication. Pressure communication is a necessary but not sufficient condition to establish flow communication. However, pressure is in communication in each primary sand body. The case was used to test the methodology proposed in this work.

The composition (analyzed to C<sub>30+</sub>) as well as saturate, aromatics, resin, and asphaltene (SARA) analysis data were measured at different depths in the laboratory. The laboratory-measured compositions were then lumped into the DFA-like five components/groups (CO<sub>2</sub>, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>–C<sub>5</sub> and C<sub>6+</sub>, referred to as pseudo-DFA data). The weight percentages of the five lumped components/groups were the inputs of the EOS model. The SARA analysis and the DFA coloration (optical density, OD) data were applied to determine the relationship between asphaltene contents in stock-tank oil (STO) and DFA coloration measured at downhole conditions. The linear relation was obtained by Betancourt *et al.* [2]:  $OD = 0.38 \times \text{wt\%} + 0.0059$ , with a small offset at the origin due to some coloration of the resin fraction.

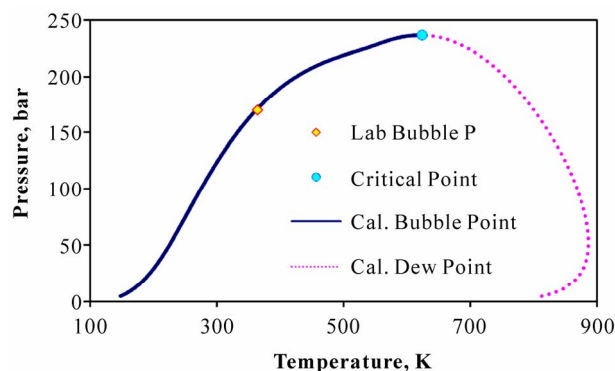
Based on the compositions of the five lumped components/groups and asphaltene content at a relative depth of 1,555 m in the M21B sand (reference DFA station), as well as the delumping and characterization method of Zuo *et al.* [25], the pseudo-DFA data were delumped and characterized to full C<sub>30+</sub> compositions. The delumped composition is compared with the gas chromatography (GC) data as shown in **Figure 1**. The agreement is good between the delumped and GC data. The physical properties and binary interaction parameters were generated which are required in the EOS calculation.



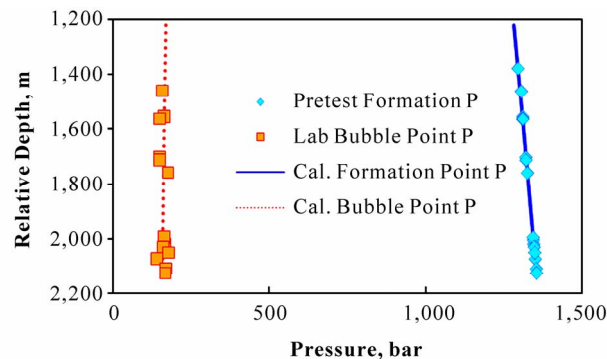
**Figure 1.** Comparison of GC and delumped compositions at the reference depth for Case 1. The delumped compositions are in good agreement with the GC data. The delumped compositions are used as inputs to the asphaltene gradient analysis.

The predicted phase envelope of this fluid as depicted in **Figure 2** indicates the formation condition is far away from its critical and bubblepoints (the formation pressure is ~1400 bar). According to the observation of Hoier and Whitson [4], it is expected that the fluids have slight compositional and property grading with depth because the fluids are hardly compressible and highly undersaturated.

It is assumed that the reservoir is isothermal and there is no external flux. Compositional gradients with depth were estimated in terms of the pseudo-DFA data at a relative depth of 1,555 m (reference depth) by solving Equation (6) without external fluxes and temperature gradients. The predicted formation and bubblepoint pressures are compared in **Figure 3** with the pretest and laboratory data. The results show that the predicted formation and bubblepoint pressures agree very well with the measurements.



**Figure 2.** Phase envelope for fluid in Case 1. The predicted bubble point is close to the experimental data. The formation conditions ( $P = \sim 1400$  bar) is far away from the critical and bubble points. Slight compositional gradients are expected according to the Hoier and Whitson [4] theory.



**Figure 3.** Comparison of predicted and measured bubble point and formation pressure for Case 1. The predictions are in accord with the measurements. The formation pressures are much higher than the bubble points. Slight compositional gradients are anticipated according to the Hoier and Whitson [4] theory.

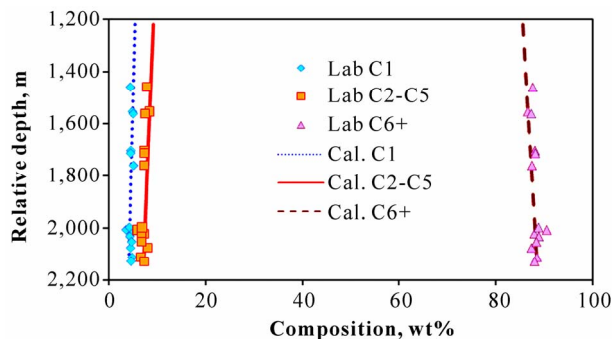
The predicted compositions are compared with the measurements as shown in **Figure 4**. Good agreement is obtained between the measurements and the predictions.

The compositional gradients of the reservoir fluids with depth are small in the Tahiti reservoir. Therefore, it is difficult to determine whether the fluid is in equilibrium or in different compartments using the traditional compositional grading method [3] because the variation of bulk fluid properties (except asphaltenes) is not evident. However, the asphaltene gradient in the column can be used for determining whether the reservoir is in equilibrium or is disconnected because asphaltenes are the heaviest components in crude oil and appear in nanoaggregates (<10 monomers). In the equilibrium model, asphaltenes have the greatest grading in crude oil owing to a gravitational segregation, although other components do not have significant gradient with depth. Furthermore, asphaltene contents are usually low in crude oil and have little impact on the bulk fluid properties such as GOR, light-end composition, and/or density. As viscosity soon joins the pantheon of DFA measurements, asphaltene content can be crosscorrelated to viscosity.

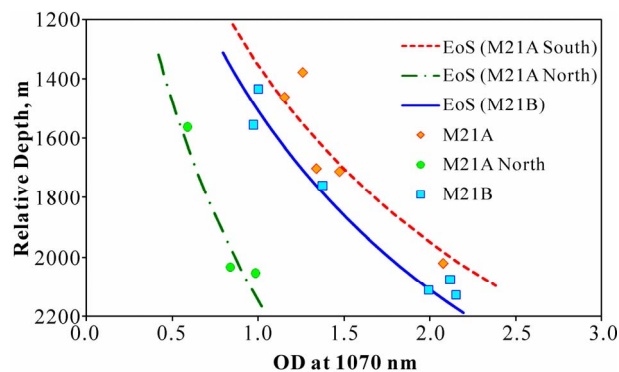
Since the Tahiti fluids are highly undersaturated black oil with very high formation pressure (~1400 bar) which is much greater than asphaltene onset pressure and relative low asphaltene content (<5 wt%), there is no asphaltene precipitation/deposition (*i.e.*, asphaltenes are stabilized) at downhole conditions. Therefore, there exist no clusters of asphaltene nanoaggregates but asphaltene nanoaggregates. The average molar mass of the asphaltene nanoaggregates in the distribution function at the reference depth was adjusted to match the coloration variation data measured by DFA. The adjusted average molar mass of the asphaltene nanoaggregates is 1,602 g/mol corresponding to ~2 nm in diameter.

**Figure 5** shows the predicted optical density (OD) variations and DFA measurements with depth. The results are similar to those obtained by Betancourt *et al.* [2] using the Boltzmann distribution equation. The coloration analyses also indicate that the sands of M21A (center), M21A North, and M21B are in different compartments. In the paper of Betancourt *et al.* [2], detailed discussions were given with regard to reservoir connectivity and coloration log predictions. The ideas are employed in this work as well.

The same fitted molar mass of the asphaltene nanoaggregate component is suitable for the entire reservoir. This means that asphaltenes have the same average size in nanoaggregates in the oil column. Most of the data from the field lies on the theoretical fit curves obtained from the EOS model of asphaltene nanoaggregates. The GOR of the crude oil is low so relatively uniform. Therefore, the entire field has the same asphaltene gradient, but



**Figure 4.** Compositional variations with depth for Tahiti fluids in Case 1. The predictions are in good agreement with the experimental data. The compositional gradients are small with depth, which has confirmed the Hoier and Whitson [4] theory.



**Figure 5.** Optical density variations with depth for Case 1. The lines denote the EOS calculations using an average asphaltene molar mass of 1602 g/mol. The symbols stand for the measurements by Live Fluid Analyzer (LFA). Sand M21A is disconnected with Sand M21B. Sand M21A North is not connected with main Sand M21A. The subsequent production data confirmed that the reservoir connectivity is implied when the reservoir asphaltenes are in equilibrium.

the north part of M21A has a much lower asphaltene concentration than the south and centric parts of M21A. As mentioned by Betancourt *et al.* [2], after a careful review of the seismic data, it is plausible that the north part of M21A is disconnected from the M21A sand (center). The M21B sand is in a different compartment than the M21A sands as determined by the formation pressure gradient and geochemistry fingerprinting of the crude oil samples; the coloration analysis is consistent in this assessment, as seen in **Figure 5**. The subsequent production data from this field confirmed that the reservoir connectivity is implied when the reservoir asphaltenes are in equilibrium.

### Case 2

Recently, Betancourt *et al.* [7] reported that black oil in a 200-m vertical column was analyzed by DFA and advanced laboratory analytical chemistry methods. The

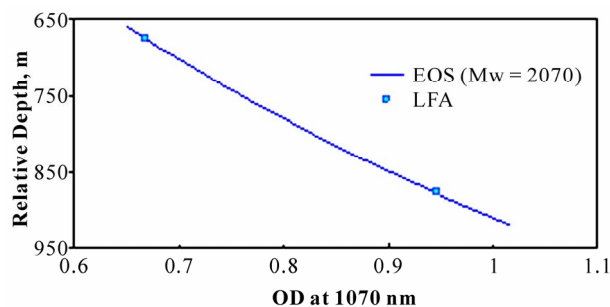
oil samples were taken from two wells with low and similar GOR of  $\sim 125 \text{ m}^3/\text{m}^3$ ; the shallower sample PER-1 is from a depth of  $\times 674 \text{ m}$ , the deeper sample PER-2 is from  $\times 874 \text{ m}$ . This is also highly undersaturated black oil whose critical point and bubble point is far away from formation conditions. The asphaltene content in stock tank oil (STO) was analyzed by a standard n-heptane precipitation method. This case was also used to test the methodology proposed in this work. Similar to the Tahiti field, the compositional and property gradients are small according to both the laboratory measurements and the EOS model. The fluids are highly undersaturated and rather incompressible; therefore, the hydrostatic head pressure in the reservoir does little to impact a compositional variation. Instead of the absolute pressure, it is the relative pressure difference in the 200-m vertical column of oil that plays an important role in generating gradients. It is impossible to conclude whether or not the oil column is connected in terms of the traditional compositional grading method. Again, coupling the asphaltene gradient analysis with the other advanced chemical analyses could give a conclusion.

If it is assumed that the reservoir is isothermal and there is no external flux, the average asphaltene molar mass is adjusted to the DFA coloration data. The adjusted value is  $2070 \text{ g/mol}$ . **Figure 6** shows coloration variations with depth. The EOS coloration analysis shows the sands in the oil column are connected and the black oils are in equilibrium. The two sands were shown to be in pressure communication, a necessary but insufficient condition to establish flow communication on production time scales. The two black oils have similar low GORs, which is consistent with their being in equilibrium. Furthermore, the reservoir sand properties are consistent with the contained fluids being in equilibrium. The primary reservoir sand has permeability of  $\sim 1$  darcy, which favors convective mixing (much faster than diffusive mixing). These conditions are very similar to those in the Tahiti reservoir, which also appeared to be in equilibrium. The other advanced chemical analyses gave the same conclusion as described by Betancourt *et al.* [7].

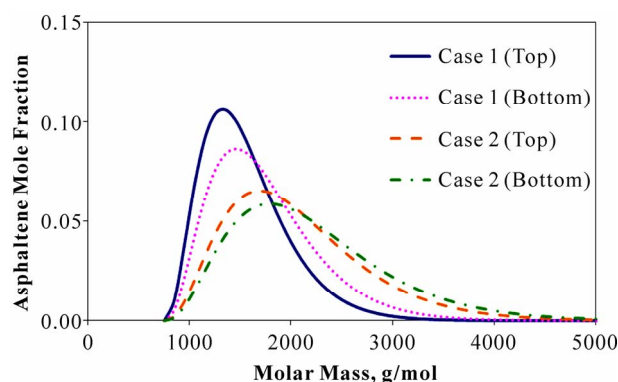
**Figure 7** shows the molar mass distribution of asphaltenes at the top and bottom of sands for both case studies. It can be seen that more heavy asphaltenes distributed at the bottom of sands in both cases. Nevertheless, the distribution changes are relatively slight even in a reservoir with as much as  $\sim 1000 \text{ m}$  vertical depth. Therefore, for simplicity, it is reasonable to assume that asphaltenes have average properties such as molar mass in entire oil columns.

## 5. Conclusions

This paper presented a methodology to analyze asphaltene



**Figure 6.** Optical density variations with depth for Case 2. The solid line represents the EOS calculation using an asphaltene average molar mass of  $2070 \text{ g/mol}$  at the reference depth. The squares are the measurements by Live Fluid Analyzer (LFA). The equilibrium nanoaggregate asphaltene profiling indicates that the reservoir is connected. The results are confirmed by the advanced chemical analysis (2-D GC) as shown in [7].



**Figure 7.** Molar mass distributions of asphaltenes for both Cases I and II. The bottom of reservoirs consists of more heavy asphaltenes than the top. The reservoir vertical thickness is  $\sim 1000 \text{ m}$  in Case I and  $\sim 200 \text{ m}$  in Case II. Both cases show variations of average asphaltene molar masses from top to bottom are small. For simplicity, it is reasonable to assume that asphaltenes have average properties such as molar mass in entire oil columns.

grading with depth using the EOS approach and the DFA tools. The inputs are the DFA measurements such as  $\text{CO}_2$ ,  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$ – $\text{C}_5$ ,  $\text{C}_{6+}$ , and the coloration associated with asphaltene contents. The delumping and characterization procedures proposed by Zuo *et al.* (2008) were applied to obtain the detailed compositions including asphaltenes and the parameters of the EOS model. Fluid-profile and coloration logs were computed by tuning the molar mass of asphaltenes against the DFA coloration logs. The methodology has been successfully applied to two cases. The results obtained in this work demonstrate that the proposed method provides a useful tool to reduce the uncertainties related to reservoir compartmentalization and to optimize the DFA logging during acquisition.

In addition, the results show that the treatment of part

of the  $C_{n+}$  fraction as an asphaltene component (monomer) in the traditional cubic EOS approach is contradicted by the recent observations that asphaltenes are dispersed as nanoaggregates in crude oils. For simplicity, it is reasonable to assume that asphaltenes have average properties such as molar mass in entire oil columns.

## REFERENCES

- [1] C. Mullins, S. S. Betancourt, M. E. Cribbs, J. L. Creek, F. X. Dubost, A. Ballard and L. Venkataraman, "Asphaltene Gravitational Gradient in a Deepwater Reservoir as Determined by Downhole Fluid Analysis," Paper SPE 106375 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 28 February–2 March 2007.
- [2] S. S. Betancourt, F. X. Dubost, O. C. Mullins, M. E. Cribbs, J. L. Creek and S. G. Mathews, "Predicting Downhole Fluid Analysis Logs to Investigate Reservoir Connectivity," Paper SPE IPTC 11488 presented at IPTC, Dubai, UAE, 4-6 December 2007.
- [3] J. Y. Zuo, O. C. Mullins, C. Dong, D. Zhang, M. O'Keefe, F. X. Dubost, S. S. Betancourt, and J. Gao, "Integration of Fluid Log Predictions and Downhole Fluid Analysis," Paper SPE 122562 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, Indonesia, 4-6 August 2009.
- [4] L. Hoier and C. Whitson, "Compositional Grading-Theory and Practice," *SPE Reservoir Evaluation & Engineering*, Vol. 4, 2001, pp. 525-535.
- [5] O. C. Mullins, G. Fujisawa, M. N. Hashem and H. Elshahawi, "Coarse and Ultra-Fine Scale Compartmentalization by Downhole Fluid Analysis Coupled," Paper SPE IPTC 10034 presented at IPTC, Doha, Qatar, 21-23 November 2005.
- [6] K. Indo, J. Ratulowski, B. Dindoruk, J. Gao, J. Zuo and O. C. Mullins, "Asphaltene Nanoaggregates Measured in a Live Crude Oil by Centrifugation," *Energy & Fuels*, Vol. 23, 2009, pp. 4460-4469.
- [7] S. S. Betancourt, G. T. Ventura, A. E. Pomerantz, O. Viloria, F. X. Dubost, J. Zuo, G. Monson, D. Bustamante, J. M. Purcell, R. K. Nelson, R. P. Rodgers, C. M. Reddy, A. G. Marshall and O. C. Mullins, "Nanoaggregates of Asphaltene in a Reservoir Crude Oil and Reservoir Connectivity," *Energy & Fuels*, Vol. 23, 2009, pp. 1178-1188.
- [8] A. Hirschberg, "Role of Asphaltene in Compositional Grading of a Reservoir's Fluid Column," *Journal of Petroleum Technology*, Vol. 40, No. 1, 1988, pp. 89-94.
- [9] J. Y. Zuo, O. C. Mullins, C. Dong, S. S. Betancourt, F. X. Dubost, M. O'Keefe and D. Zhang, "Investigation of Formation Connectivity Using Asphaltene Gradient Log Predictions Coupled with Downhole Fluid Analysis," Paper SPE 124264 presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 4-7 October 2009.
- [10] L. X. Nghiem, M. S. Hassam and R. Nutakki, "Efficient Modeling of Asphaltene Precipitation," Paper SPE 26642 presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, 3-6 October 1993.
- [11] L. X. Nghiem and D. A. Coombe, "Modeling Asphaltene Precipitation during Primary Depletion," Paper SPE 36106 presented at the SPE IV Latin American/Caribbean Petroleum Engineering Conference, Trinidad and Tobago, 23-26 April 1996.
- [12] X. Qin, P. Wang, K. Sepehrnoori and G. Pope, "Modeling Asphaltene Precipitation in Reservoir Simulation," *Industrial Engineering Chemistry Research*, Vol. 39, 2000, pp. 2644-2654.
- [13] K. S. Pedersen and P. L. Christensen, "Phase Behavior of Petroleum Reservoir Fluids," CRC Press, Taylor & Francis Group, Boca Rston, Florida, 2007.
- [14] A. Gisolf, F. X. Dubost, J. Zuo, S. Williams, J. Kristoffersen, V. Achourov, A. Bisarah and O. C. Mullins, "Real Time Integration of Reservoir Modeling and Formation Testing," Paper SPE 121275 presented at the EUROPEC/EAGE Annual Conference and Exhibition, Amsterdam, 8-11 June 2009.
- [15] A. E. Pomerantz, M. R. Hammond, A. L. Morrow, O. C. Mullins and R. N. Zare, "Asphaltene Molecular-Mass Distribution Determined by Two-Step Laser Mass Spectrometry," *Energy & Fuels*, Vol. 23, No. 3, 2009, pp. 1162-1168.
- [16] O. C. Mullins, B. Martinez-Haya and A. G. Marshall, "Contrasting Perspective on Asphaltene Molecular Weight. This Comment vs. the Overview of A. A. Herod, K. D. Bartle, and R. Kandiyoti," *Energy & Fuels*, Vol. 22, No. 3, 2008, pp. 1765-1773.
- [17] O. C. Mullins, "The Physics of Reservoir Fluids: Discovery through Downhole Fluid Analysis," Schlumberger, Sugar Land, Texas, 2008.
- [18] C. H. Whitson, T. F. Anderson and I. Sorede, "Application of the Gamma Distribution Model to Molecular Weight and Boiling Point Data for Petroleum Fractions," *Chemical Engineering Communications*, Vol. 96, 1990, pp. 259-278.
- [19] C. H. Whitson, T. F. Anderson and I. Soreide, "C<sub>7+</sub> Fraction Characterization," in: L. G. Chorn and G. A. Mansoori, Ed., Taylor & Francis New York Inc., New York, 1989, p. 35.
- [20] C. H. Whitson, "Effect of C<sub>7+</sub> Properties on Equation of State Predictions," *Soc. Pet. Eng. J.*, December 1984, pp. 685-696.
- [21] A. K. Tharanivasan, W. Y. Svrcek, H. W. Yarranton, S. D. Taylor, D. Merino-Garcia and P. Rahimi, "Measurement and Modeling of Asphaltene Precipitation from Crude Oil Blends," *Energy and Fuels*, Vol. 23, 2009, pp. 3971-3980.
- [22] F. Montel, J. Bickert, A. Lagisquet and G. Galliero, "Initial State of Petroleum Reservoirs: A Comprehensive Approach," *Journal of Petroleum Science and Engineering*, Vol. 58, 2007, pp. 391-402.
- [23] K. S. Pedersen and N. Lindeloff, "Simulations of Compositional Gradients in Hydrocarbon Reservoirs under the Influence of a Temperature Gradient," Paper SPE 84364



- presented at the SPE Annual Technical Conference and Exhibition, Denver, Colorado, 5-8 October 2003.
- [24] J. Y. Zuo and D. Zhang, "Plus Fraction Characterization and PVT Data Regression for Reservoir Fluids near Critical Conditions," Paper SPE 64520 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Brisbane, Australia, 16-18 October 2000.
- [25] J. Y. Zuo, D. Zhang, F. Dubost, C. Dong, O. C. Mullins, M. O'Keefe and S. S. Betancourt, "EOS-Based Downhole Fluid Characterization," Paper SPE 114702 presented at the SPE Asia Pacific Oil & Gas Conference and Exhibition, Perth, Australia, 20-22 October 2008.
- [26] K. Akbarzadeh, A. Dhillon, W. Y. Svrcek and H. W. Yarranton, "Methodology for the Characterization and Modeling of Asphaltene Precipitation from Heavy Oils Diluted with n-Alkanes," *Energy & Fuels*, Vol. 18, 2004, pp. 1434-1441.
- [27] H. Alboudwarej, K. Akbarzadeh, J. Beck, W. Y. Svrcek and H. W. Yarranton, "Regular Solution Model for Asphaltene Precipitation from Bitumens and Solvents," *AIChE Journal*, Vol. 49, 2003, pp. 2948-2956.
- [28] J. X. Wang and J. S. Buckley, "A Two-Component Solubility Model of the Onset of Asphaltene Flocculation in Crude Oils," *Energy & Fuels*, Vol. 15, 2001, pp. 1004-1012.