

A Stochastic Model for the Fractal Dimension Estimation of Asphaltenes Aggregation

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Abstract: Some of the problems associated with the transportation of crude oils are due to the presence of heavy compounds as asphaltene molecules. This work developed a stochastic model that predicts the fractal dimension of the asphaltene aggregates. It was found that the maximum value of the fractal dimension is 1.71, which corresponds to the reported experimental results. The model can be applied as a universal growing behavior for the analysis of surface roughness when solids deposition is observed in the production systems involving crude oils.

Index Terms: 2D and 3D observation, fractal dimension estimation, aggregation/segregation processes.

I. INTRODUCTION

Through liquids characterization, some possible physical changes and transport conditions can be predicted when working with crude oils [1] since is known that asphaltenes are one of the various kinds of compounds in the crude and which could have different structural conformations [2,3].

If a chemical is added to a crude oil system, the aggregates microstructural behavior will depend on the kind of chemical and the effect that it has on the system, but, even when such aggregates could diffuse into a compatible medium, the main structure and conformation of the aggregates will remain unchangeable [4]. On the other hand, there are some products based on natural amphiphilic phenols that modify the viscosity by dispersing asphaltenes [5,6]. Some copolymers can also modify the flow capacity in a pipeline without compromise a viscosity modification [7] by varying the alkali chains and producing a reduction of the aggregates even if the conditions of the system favor the precipitation process [8]. In general, the morphology of the crystalized solids is attributed to the polarity of the molecules involved in such a process [9]. At the macroscopic level, there are numerical simulation methods to estimate and predict the fluid flow and

its behavior concerning other processes, e.g., heat exchanges [10]. However, to work out the estimations, it is necessary the rheologic characterization of the medium, and it must consider if the liquid behavior is Newtonian or non-Newtonian [11,12]. The concentration of the asphaltenes and resins that constitute a crude oil take part on the interfacial tension value for transporting medium or to the liquid joined to it, and the properties of these kinds of molecules (like aromaticity) is also relevant [13]. It has been addressed that the main cause of solids formation in crude oils is due to the aggregation of the heaviest components (asphaltenes, paraffin, and both in combination). A way to explain their microscopic morphology is through fractal dimension and the diffusion-limited aggregation [14] that has been quite yet simulated [15]. Despite the knowledge acquired, formation condition, prevention, and overcoming of the formation while the liquid moves through a pipeline are some of the issues under study that must be understood [16]. According to the above, asphaltene molecules tend to group to form aggregates, which in turn tend to precipitate, causing several and expensive operational issues [17,18]. The present work proposes the use of mesoscopic modeling technics based on a master equation to predict the dependency between aggregates fractal dimension and the dynamic processes of aggregation and segregation that occur at the individual molecule level. The starting point of the modeling is the consideration that the irregular and complex character of the morphology of the aggregates is due to the intrinsically stochastic character of the aggregation/segregation processes at the same single level.

II. MATERIALS AND METHODS

A. Preliminary considerations

The next conditions were established to obtain the mesoscopic model that describes the formation of a single asphaltene aggregate:

1) The microscopic variable that describes the system behavior is the N number of asphaltene molecules that constitute the aggregated

2) The system is visualized in 2 or 3 dimensions (2D or 3D). In the first case, the macroscopic variable is the N fraction of the total area (in the aggregated) occupied by asphaltenes, and for the second case, this variable refers to the volume fraction in such a way that:

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$$n = \frac{\alpha N}{\Omega} \quad (1) \quad N : \frac{\Delta N}{N} \approx 0 \quad (8)$$

where

$$\begin{aligned} 2D : \Omega &= \pi R^2 : \alpha = a \\ 3D : \Omega &= \frac{4}{3} \pi R^3 : \alpha = v \end{aligned} \quad (2)$$

And a and v represent, respectively, the area and volume of a single molecule and R is the aggregated maximum radio.

3) At the macroscopic level, it is considered that two fundamental processes occur. The aggregation process, in which $N \rightarrow N+1$ where a free asphaltene molecule interacts with an aggregated molecule and joins to it to form part of the aggregated, having a transition probability per unit of time as:

$$W_{N+1/N} = \frac{k_a}{\Omega} N_0 N \quad (3)$$

Where k_a is the transition velocity constant per unit of time and N_0 is the number of free asphaltene molecules. The second process is segregation, where $N \rightarrow N-1$ and for which the transition probability per unit of time is supposed as:

$$W_{N-1/N} = K_d N \quad (4)$$

where K_d represents the segregation velocity constant, which a priori is supposed to depend on the area fraction covered by the asphaltene molecules:

$$K_d = k_d \frac{N}{\Omega} \quad (5)$$

B. Master equation deduction

From the considerations established in section A, a master equation (ME) is obtained, and this describes the temporary behavior of the probability $P(N;t)$ that exist N asphaltene molecules at the time t :

$$\begin{aligned} \frac{\partial P(N;t)}{\partial t} &= (\mathbf{E}_N^{-1} - 1) \frac{k_a}{\Omega} N_0 N P(N;t) + (\mathbf{E}_N^{+1} - 1) k_d \frac{N^2}{\Omega} P(N;t) \\ P(N_0;0) &= 1 \end{aligned} \quad (6)$$

where E_N^a is the ascent-descent operator that acts on the discrete variable functions:

$$\mathbf{E}_N^a [f(N)] = f(N + a) \quad (7)$$

C. Master equation solution

The ME is a differential equation in differences, nonlinear about the transition probabilities per unit of time, and therefore, it does not have an exact analytical solution. However, it is possible to obtain an approximated analytical solution if it is considered that the change ΔN in the N number of molecules when an individual microscopic process occurs is negligibly faced to

So that, N can be considered as a continuous variable. By expressing the ascent-descent operator in its differential form, it is obtained the equivalent Fokker-Planck equation (FPE):

$$\begin{aligned} \frac{\partial P(N;t)}{\partial t} &= - \frac{\partial}{\partial N} \left\{ \left(\frac{k_a}{\Omega} N_0 N - k_d \frac{N^2}{\Omega} \right) P(N;t) \right\} \\ &+ \frac{1}{2} \frac{\partial^2}{\partial N^2} \left\{ \left(\frac{k_a}{\Omega} N_0 N + k_d \frac{N^2}{\Omega} \right) P(N;t) \right\} \end{aligned} \quad (9)$$

For the FPE, expressed as a function of the intensive macroscopic variables, it is obtained that:

$$\frac{\partial P(n;t)}{\partial t} = - \frac{\partial}{\partial n} \{ (k_a n_0 n - k_d n^2) P(n;t) \} + \frac{\alpha}{\Omega} \frac{1}{2} \frac{\partial^2}{\partial n^2} \{ (k_a n_0 n + k_d n^2) P(n;t) \} \quad (10)$$

Where, closer to the steady-state, the probability function $P(n;t)$ can be established as a normal o Gaussian, so it is enough to determine the expected value behavior and the variance to describe the stochastic process. From the FPE, the expected value $\langle n \rangle$ is:

$$\begin{aligned} \frac{d\langle n \rangle}{dt} &= k_a n_0 \langle n \rangle - k_d \langle n \rangle^2 \\ \langle n \rangle_0 &= n_0 \end{aligned} \quad (11)$$

and the variance of the fluctuations around this expected value:

$$\begin{aligned} \frac{d\sigma}{dt} &= 2(n_0 k_a - 2\langle n \rangle k_d) \sigma + \frac{1}{\Omega} (k_a n_0 \langle n \rangle + k_d \langle n \rangle^2) \\ \sigma(0) &= 0 \end{aligned} \quad (12)$$

Therefore, for the steady-state:

$$\langle n \rangle = \kappa \quad (13)$$

$$\sigma = \frac{\alpha}{\Omega} \frac{(\langle n \rangle^2 + \langle n \rangle \kappa)}{(4\langle n \rangle - 2\kappa)} \quad (14)$$

where the parameter κ represents the product of the free asphaltene concentration and the aggregation-segregation velocity constants ratio:

$$\kappa = \frac{n_0 k_a}{k_d} \quad (15)$$

At the macroscopic scale, the variance is expressed by:

$$\sigma = \frac{\alpha}{\Omega} \langle n \rangle \tag{16}$$

The probability distribution function is given by:

$$P(n) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{(n - \langle n \rangle)^2}{(2\sigma)}\right) \tag{17}$$

Equation (17) constitutes the mesoscopic model describing the area/volume fractions behavior that is occupied by the asphaltene molecules in the aggregated.

III. RESULTS AND DISCUSSION

In the mesoscopic model, the magnitude of the intern fluctuations is scaled up to the system size in such a way that when this is bigger than the size of an individual molecule, the fluctuations are negligible compared to the expected value. Due to the fractal morphology of the conglomerated is a manifestation of the intern fluctuations which have their origin in the stochastic character of the aggregation/segregation microscopic processes, its characterization requires to observe the system in level small enough to have a comparable value between the intern fluctuations and the expected value. Theoretically, this is modeled by writing the variance as a function of the parameter ε , that is related to the fractal dimension by:

$$\varepsilon = \frac{\alpha}{\Omega} \tag{18}$$

considering that:

$$\langle n \rangle_{N \rightarrow 1} \sim \varepsilon \tag{19}$$

the variance equation is:

$$\sigma = \varepsilon \frac{(\varepsilon^2 + \varepsilon\kappa)}{(4\varepsilon - 2\kappa)} \tag{20}$$

It is convenient to express the variance as a power function of ε , as:

$$\sigma \sim \varepsilon^\beta \tag{21}$$

for which, ratio (22) is applied:

$$\beta = \lim_{\varepsilon \rightarrow 1} \left(\frac{d \ln \sigma}{d \varepsilon} \right) \left(\frac{d \ln \varepsilon}{d \varepsilon} \right)^{-1} \tag{22}$$

obtaining:

$$\beta = \frac{(2\kappa^2 + \kappa - 4)}{(\kappa^2 - \kappa - 2)} \tag{23}$$

$$\kappa \in [0;1]$$

Then, the probability function is written as:

$$P(\langle n \rangle_{N \rightarrow 1}) = P(\varepsilon) = \frac{1}{\sqrt{2\pi\varepsilon^\beta}} \exp\left(-\frac{(\varepsilon - \langle \varepsilon \rangle)^2}{2\varepsilon^\beta}\right) \tag{24}$$

For the steady-state, it is achieved the ergodicity property, which means that the average values are equal to the averages of the set. In this way, if the probability is seen from the set, its expected value is equivalent to the density ρ of asphaltenes present in the area/volume observed fraction, so that:

$$\rho = \int P(\varepsilon)P(\varepsilon)d\varepsilon$$

$$= \frac{1}{\sqrt{2\pi\varepsilon^\beta}} \exp\left(-\frac{(\langle \varepsilon \rangle - \langle \varepsilon \rangle)^2}{2\varepsilon^\beta}\right)$$

$$= 0.4\varepsilon^{-0.5\beta} \tag{25}$$

Defining $\Phi = K\varepsilon^f$ as the matter content confined in a given space, being f the fractal dimension and K a constant that depends on the system observing scale, for a 2D observation of the system inside a circle with radius R :

$$\Phi = \int_0^{2\pi} \int_0^R \rho(\varepsilon)\varepsilon d\varepsilon d\theta$$

$$= \int_0^{2\pi} \int_0^R \rho(\varepsilon)\varepsilon d\varepsilon d\theta$$

$$= K\varepsilon^{(2-0.5\beta)} \tag{26}$$

then:

$$2D : f = \frac{1}{2} \frac{2\kappa^2 - 5\kappa - 4}{(\kappa + 1)(\kappa - 2)} \tag{27}$$

And for the 3D observation of the system contained in a sphere with radius R :

$$\Phi = \int_0^{2\pi} \int_0^\pi \int_0^R \rho(\varepsilon)\varepsilon^2 \sin \phi d\varepsilon d\phi d\theta$$

$$= K\varepsilon^{(3-0.5\beta)} \tag{28}$$

then:

$$3D : f = \frac{1}{2} \frac{4\kappa^2 - 7\kappa - 8}{(\kappa + 1)(\kappa - 2)} \tag{29}$$

Figures 1 and 2 show the fractal dimension behavior of the aggregated of asphaltene molecules when it is seen in 2D and 3D, respectively.

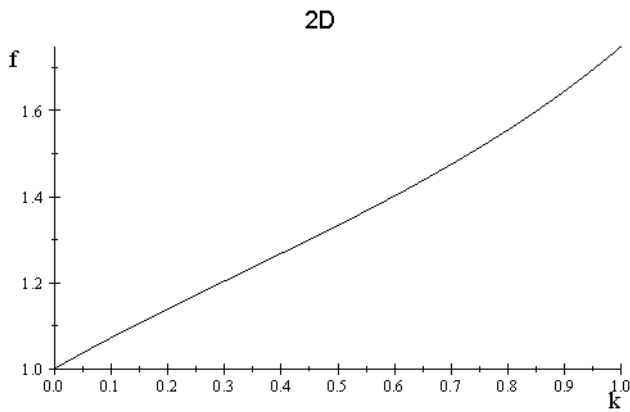


Figure 1. 2D behavior of the fractal dimension f of an asphaltene aggregated concerning κ (eq. 27).

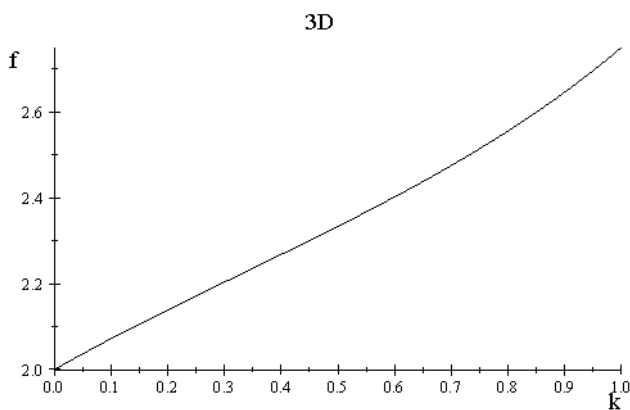


Figure 2. 3D behavior of the fractal dimension f of an asphaltene aggregated concerning κ (eq. 29).

IV. CONCLUSIONS

From the definition of the preliminary considerations, it was proposed a stochastic model to emulate the fractal dimension of an asphaltene conglomeration. It was found that the developed model predicts that the maximum reachable fractal dimension value for this kind of deposition is around 1.71, which corresponds to diffusion-limited aggregation (DLA) growth kind and is in concordance with the experimental results obtained for other authors supporting the hypothesis that the ramifications of the aggregates will be characterized in the same form despite the size of the conglomerate. The main repercussions of this study are centered on the existence of a possible universality of the aggregates growth that could be applied in roughness surface analysis. This work also allows observing that, when there is asphaltene deposition, is not possible to obtain a flat surface; therefore it can be hypothesized that, for this case, the friction factor is increased as well as in the case of viscosity when it is observed a high concentration of asphaltenes in the crude oils.

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