Chemical Physics 517 (2019) 6–12

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Particles aggregation and fragmentation — A Monte Carlo study

Mohsen Zirrahi[a], Bahareh Azinfar[a], Hassan Hassanzadeh[a,*], Jalal Abedi[a], Reza Azin[b], Shahriar Osfouri[c]

[a] Department of Chemical & Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada
[b] Faculty of Petroleum, Gas and Petrochemical Engineering, Persian Gulf University, Bushehr, Iran
[c] Department of Chemical Engineering, Persian Gulf University, Bushehr, Iran

ARTICLE INFO

Keywords:
Asphaltene precipitation
Aggregation
Asphaltene onset
Monte Carlo molecular simulation
Scaling relation

ABSTRACT

Molecular simulation of particles aggregation is a time-intensive computation. In this study, we have developed a computational methodology to simulate the aggregation and fragmentation of particles. Scaling relations are developed that can be used to decrease the number of primary particles towards minimization of the computation time. The developed methodology is applied to reproduce the experimental data of particles aggregation and fragmentation. Results show the capability of the proposed methodology to represent the experimental data. Then, the model is applied to predict the onset of precipitation, the amount of precipitated particles, and their particles size distribution. The simulation results are in agreement with the experimental data. The proposed simulation methodology and the scaling relations find applications in simulation of particles aggregation and fragmentation.

1. Introduction

Aggregation and fragmentation of particles in the presence of flow are encountered in many applications such as the mixing of incompatible crude oils [1], the flow of suspensions through porous structures [2], the migration of brain tumor cells in tumor malignancy [3,4], and industrial processing of soft matter [5]. Often, mixing of two incompatible crude oils leads to appearance of nano-sized particles [1] or so called asphaltene as a result of thermodynamic destabilization. Under favorable conditions these nanoparticles will eventually aggregate and precipitate. Kinetic of particle aggregation is very important for prediction of the onset of precipitation and particle size distribution.

Asphaltenes precipitation, which results when two incompatible crude oils are mixed, is traditionally modeled as a π-π interaction between monomers with size of ~1 nm to form a nano-aggregate. The driving forces resulting in asphaltene aggregation usually possess electrostatic (such as hydrogen bonding) or dispersive (θ-θ, θ-π, and π-π interactions) nature. The π-π interaction was mentioned as the major driving force for asphaltene aggregation. Each nano-aggregate is assumed to contain 5–10 monomers with size of ~5 nm. Then, the nano-aggregates aggregate to form the asphaltene particles with size of higher than 1 μm. Each particle may contain more than 10^8 monomers of asphaltene [6–8]. The majority of studies on particle aggregation have utilized the Smoluchowski's equation or modified versions of this population balance equation (PBE) [9–11]. This approach is very computationally intensive since an ordinary differential equation (ODE) should be solved for each particle. For instance, when this equation should be solved for 10^5 particles, 10^5 ODEs should be solved simultaneously. Solution of this system of equations becomes impossible when the ratio of diameter of the final to the primary particle increases [12]. Geometric population balance equations are a solution to reduce the number of ODEs that should be solved [11,13,14]. However, the material balance (i.e. mass balance) error is an inevitable problem associated with the numerical solution of ODEs. Choosing an appropriate time step needs consideration of many parameters such as initial population and number of ODEs and also requires several trial and error calculations.

In this work, we use Gillespie [15] methodology to solve the population balance equation. This methodology uses Monte Carlo procedure to simulate the time evolution of particles population. The Gillespie method is a Monte Carlo derived technique for exact stochastic simulation. Implementation of a stochastic simulation method results in more realistic representation of actual aggregation and fragmentation because these processes are stochastic in nature. There are numbers of remarkable advantages associated with Gillespie methodology. First, there is no need to define the time step for simulations. Therefore, the material balance error is minimized. Second, scaling relations can be

* Corresponding author.
E-mail address: hhassanz@ucalgary.ca (H. Hassanzadeh).

https://doi.org/10.1016/j.chemphys.2018.09.030
Received 19 June 2018; Accepted 21 September 2018
Available online 22 September 2018
0301-0104/

Nomenclature

A	particle symbol
a	reaction rate
d	particle diameter
d_0	diameter of primary unit particles
D_f	fractal dimension
F	fragmentation rate constant
f	adjustable parameter
i and j	bin number
K	aggregation rate constant
k	adjustable parameter
m	mass of particle
n_0	primary unit number
P	reaction rate probability
R	geometric scaling
r	random number
R_g	universal gas constant
T	absolute temperature
t	time
Vs	solvent volume percent
x	diameter of particles
$\overline{d}$	average diameter
α	adjustable parameter
β	collision efficiency
ε	packing factor
μ	viscosity
τ	time interval
ϕ	particle volume fraction

obtained and applied to decrease the number of initial particles required for population balance simulations. In addition, Gillespie method converges to a certain number of particles independent from their initial population.

The contribution of this work can be summarized as: development of an efficient simulation methodology for prediction of the aggregation and fragmentation of particles; development of scaling relations that can be used to find particle size distribution and the average diameter of particles without the need for running the expensive PBE simulations; evaluation of the proposed methodology using experimental data of particle aggregation of well-defined systems in reaction-limited cluster aggregation (RLCA); implementation of the developed simulation methodology to simulate asphaltene precipitation and predict the onset time of precipitation, particle size distribution (PSD) and the amount of precipitated particles.

This paper is organized as follows: first, we describe the details of the proposed methodology used in simulations. Then, theoretical predictions and scaling relations will be presented and discussed. Next, validation of the developed methodology with experimental data will be presented. Finally, application of the developed formulation for precipitation of asphaltene will be discussed followed by conclusion section.

2. Formulation of aggregation and fragmentation kinetics

Kinetics of aggregation and fragmentation of particles can be formulated using the following reactions:

$$A_i + A_j \underset{F_l}{\overset{K_{ij}}{\leftrightarrow}} A_l \tag{1}$$

where A_i shows particles in bin i. K_{ij} and F_l are the rate constants of aggregation and fragmentation, respectively.

To calculate the reaction rates, aggregation and fragmentation constants are required. There are number of approaches to define the aggregation and fragmentation constants [9,16,17]. In this work, we use the proposed collision kernel reported in the literature [12] for asphaltene containing systems where the Brownian aggregation kernel (K_{ij}) can be obtained as:

$$K_{ij} = \beta \frac{2R_g T}{3\mu} \frac{(d_i + d_j)^2}{d_i d_j} \tag{2}$$

where R_g is the universal gas constant; T is the absolute temperature and μ is the viscosity, β shows the collision efficiency and d is the particle diameter. For a constant composition system K_{ij} can be written as:

$$K_{ij} = k \frac{(d_i + d_j)^2}{d_i d_j} \tag{3}$$

where $k = 2\beta R_g T/3\mu$ can be defined as a tuning parameter. Fragmentation constant is defined as $F_l = f\Phi(l)$ [16] where Φ is a function describing the dependency of fragmentation constant on the lth aggregate. $F_l = f d_l^{\alpha}$ was applied in this work where f and α are the adjustable constants. In this work, we assumed only the symmetric fragmentation [9]. It means that each particle can break to two particles with equal mass. It is only possible for particles consisting even numbers of primary units.

The particle aggregation and fragmentation occur over a wide range of particle sizes. Therefore, it becomes a highly expensive computation. Geometric size domain discretization has been applied in the literature of particle aggregation and fragmentation to ease the calculations towards the practical applications. It is worth noting that the geometric size domain discretization applied in engineering studies [12,13] is an analogy to logarithmic spaced bins in physics and astronomy sciences. We applied a geometric population balance equation (PBE) with discretization described as $m_i/m_{i-1} = R$ where R is the geometric scaling and m_i is the mass of each particle in bin i. An aggregate in bin i is formed by aggregation of R^{i-1} particle of mass m_0 (the asphaltene nanoaggregates at starting time $t = 0$; so-called "primary unit") [12]. Particle diameter (d_i) is calculated as given by $d_i = (R^{i-1}/\varepsilon)^{1/D_f} d_0$ where ε is the packing factor, R is the geometric scaling, and D_f is the fractal dimension. Packing factor was assumed 0.6366 [12]. For asphaltene particles, fractal dimension of 1.65 was obtained from previous studies [18]. d_0 is diameter of the asphaltene nanoaggregates (primary unit) and was obtained from literature to be equal to 2.5 nm for asphaltene particles [12]. Assuming spherical shape of each primary unit and density of 1200 kg/m^3 for asphaltene, mass of each primary unit (m_0) can be calculated. In this work we used R = 2 where the aggregates placed in the first six bins (A_1–A_6) is formed of 1, 2, 4, 8, 16 and 32 numbers of primary units.

In this work, we simulate the particle aggregation and fragmentation using the notion of chemical reactions. This allows us to simplify the ternary and higher order reactions to elementary chemical reactions. We consider four mechanisms for generation and depletion of particles [12,13] as well as a fragmentation mechanism in each bin. In this approach, particles in bin i can form if particle in bin $i-1$ is available. Implementation of this approach reduces the reactions dramatically while the results follow reliable and reasonable trends. Table 1 summarizes the mechanisms and also shows the reaction for each mechanism. More details on generation and depletion mechanisms can be found from references [12] and [13].

As an example, the reaction paths to generate and break the aggregate A_4 can be written as:

$$2A_3 \overset{K_{33}}{\rightarrow} A_4 \tag{4}$$

$$A_3 + 2A_2 \overset{K_{32}}{\rightarrow} A_4 \tag{5}$$