

# STUDY OF CORRELATIONS FOR THE PREDICTION OF THE DIFFUSION COEFFICIENTS IN MULTICOMPONENT MIXTURE

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**ABSTRACT** – Interfacial diffusive exchanges are directly related to the diffusion coefficients. These coefficients may be obtained through experimental data or by using correlations, which should be selected according to the system conditions, such as temperature and pressure, and the chemical nature of the species in the mixture. In this work, the calculation of the diffusive rates in a two-phase flow composed by a multicomponent mixture of methane, n-pentane, n-hexane and n-octane was carried out using the effective diffusivity model. The theoretical equation of Chapman-Enskog and the empirical correlations of Gilliland, Slattery-Bird, Fuller-Schettler-Giddings (FSG) and Huang *et al.* (HEA) were applied to estimate the diffusion coefficients in vapor phase. The Euler-Lagrange approach was adopted to model the two-phase flow using CFD techniques. The results showed that the correlations predicted the diffusion coefficients with similar precision for this mixture.

## 1. INTRODUCTION

Estimation of diffusion coefficients is important in processes involving mass transfer such as distillation, extraction, combustion and spray operations. Diffusion coefficients may be obtained experimentally or estimated from correlations. There are several correlations to calculate the binary diffusion coefficients in the literature and they must be chosen according to the nature of the mixture components and physical conditions of the system of interest (Eslamloueyan and Khademi, 2010). These requirements are critical since the applicability of a correlation is restricted to the conditions at which it was developed, as well as the reliability of the estimated coefficients.

Based on these statements, in this work different correlations for the prediction of diffusion coefficients in finite concentrations in a vapor phase composed by methane, n-pentane, n-hexane and n-octane were studied. The effective diffusivity model was used to calculate the interfacial diffusive flux. Thus, a code in C language was implemented and dynamically coupled to the commercial code ANSYS<sup>®</sup> CFD (FLUENT<sup>®</sup>) version 14.0. The system was composed by a two-phase flow modeled according to the Euler-Lagrange approach, i.e., liquid phase is dispersed in the form of droplets in a continuous vapor phase. The composition and temperature profiles obtained by employing each of the correlations were compared and results were analyzed.

## 2. MATHEMATICAL MODEL

The implemented model to calculate interfacial diffusive flux was based on the effective diffusivity model, where the fluxes are obtained according to Fick's law. The effective diffusion coefficient ( $D_{eff,i}$ ) represents the interactions between species  $i$  and all the species that compose the mixture, being written as (Taylor and Krishna, 1993):

$$D_{eff,i} = (1 - x_i) \left( \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{D_{ij}^{MS}} \right)^{-1}, \quad (1)$$

where  $x_i$  is the molar fraction of species  $i$  and  $D_{ij}^{MS}$  is the Maxwell-Stefan diffusion coefficient (MSC) ( $\text{m}^2 \cdot \text{s}^{-1}$ ). MSC are obtained through the generalized Vignes correlation (Wesselingh and Krishna, 1990) along with the model of Kooijman and Taylor (1991):

$$D_{ij}^{MS} = (D_{ij}^{\infty})^{x_i} (D_{ij}^{\infty})^{x_j} \prod_{\substack{k=1 \\ k \neq i,j}}^n (D_{ik}^{\infty} D_{jk}^{\infty})^{x_k/2}, \quad (2)$$

where  $D_{ij}^{\infty}$  is the infinity diluted diffusion coefficients ( $\text{m}^2 \cdot \text{s}^{-1}$ ), calculated using the correlation of Leahy-Dios and Firrozabadi (2007):

$$\frac{(cD_{ij}^{\infty})}{(cD_{ij}^o)} = A_0 \left( \frac{T_{r,i} P_{r,j}}{T_{r,j} P_{r,i}} \right)^{A_1} \left( \frac{\mu}{\mu_0} \right)^{[A_2(\omega_i, \omega_j) + A_3(P_r T_r)]}, \quad (3)$$

where  $A_0$ ,  $A_1$ ,  $A_2$  and  $A_3$  are parameters estimated according to Leahy-Dios and Firrozabadi (2007),  $T_r$  and  $P_r$  are the reduced temperature (K) and the reduced pressure (Pa),  $\mu_0$  is the diluted viscosity calculated according to Stiel and Thodos correlation (Stiel and Thodos, 1961).  $D^o$  is the diffusion coefficient in finite concentrations ( $\text{m}^2 \cdot \text{s}^{-1}$ ), which was obtained using the following equations:

- Chapman-Enskog theoretical equation (Bird *et al.*, 2002):

$$D_{ij} = 0.0186 \frac{T^{3/2}}{P \sigma_{ij} \Omega_D} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}, \quad (4)$$

where  $T$  is temperature (K),  $P$  is pressure (Pa),  $\sigma_{ij}$  is the collision diameter ( $\text{\AA}$ ),  $\Omega_D$  is the collision integral, and  $M_i$  is the molecular weight of species  $i$  ( $\text{kg} \cdot \text{kmol}^{-1}$ ).

- Correlation of Gilliland (Gilliland, 1934):

$$D_{ij} = 0.043 \frac{T^{3/2}}{P(V_i^{1/3} + V_j^{1/3})} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}, \quad (5)$$

where  $V_i$  is the molar volume at the boiling point ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ).

- Correlation of Huang *et al.*, 1972 (Huang *et al.*, 1972) named in this work as HEA:

$$D_{ij} = 5.06 \frac{T^{1.75}}{P^{1.286}(V_i^{1/3} + V_j^{1/3})} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}. \quad (6)$$

- Correlation of Slattery-Bird (Slattery and Bird, 1958):

$$D_{ij} = 2.745 \frac{T^{1.823} (P_{c,i} P_{c,j})^{1/3} (T_{c,i} T_{c,j})^{5/12}}{P (T_{c,i} T_{c,j})^{1.823}} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{-1/2}, \quad (7)$$

where  $T_c$  and  $P_c$  are the critical temperature (K) and critical pressure (Pa).

- Correlation of Fuller-Schettler-Giddings (FSG) (Fuller *et al.*, 1966), defined in this work as FSG:

$$D_{ij} = 0.01 \frac{T^{1.75}}{P(\sum v_i^{1/3} + \sum v_j^{1/3})} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}, \quad (8)$$

where  $v_i$  is the atomic volume of diffusion of the species  $i$ , calculated as the summation of the atomic values of individuals atoms that compose the molecular structure of species  $i$ . It should be noted that these equations are valid to nonpolar gaseous mixtures at low pressures.

The mass flow rate was calculated according to Equation 9:

$$\frac{dm_{p,i}}{dt} = M_i A_p k_m (C_{i,s} - C_{i,\infty}), \quad (9)$$

where  $A_p$  is the surface area of the droplet ( $\text{m}^2$ ),  $k_m$  is the convective mass transfer coefficient ( $\text{m} \cdot \text{s}^{-1}$ ),  $C_{i,s}$  and  $C_{i,\infty}$  are the molar concentrations of species  $i$  in the droplet surface and in the bulk of the vapor phase ( $\text{kmol} \cdot \text{m}^{-3}$ ). The parameter  $k_m$  is calculated with Equation 10:

$$k_{m,i} = \frac{Sh_i D_{eff,i}}{d_p}, \quad (10)$$

where  $Sh_i$  is the Sherwood number and  $d_p$  is the particle diameter (m).

### 3. METHODS

The commercial code ANSYS® CFD (FLUENT®) was used to perform the simulations and the double precision pressure-based solver 2D was employed with the segregated SIMPLE algorithm. Moreover, the discretization scheme of second order upwind was used to solve the convection terms. The finite volume method is used by ANSYS® CFD (FLUENT®) to solve the conservation equations (Fluent, 2011).

The Euler-Lagrange approach was applied to model the two-phase flow and the phases interact according to a two-way coupling, i.e., phases exchange mass and heat with one other through source terms. Mass, species, energy and momentum conservation equations solved for the vapor phase are presented as follow:

$$\frac{d\rho_v}{dt} + \nabla \cdot (\rho_v \vec{v}_v) = S_m, \quad (11)$$

$$\frac{\partial}{\partial t} (\rho_v Y_i) + \nabla \cdot (\rho_v \vec{v}_v Y_i) = -\nabla \cdot \vec{J}_i + S_i, \quad (12)$$

$$\frac{\partial}{\partial t} (\rho_v h_v) + \nabla \cdot (\rho_v h_v \vec{v}_v) = \nabla \cdot \left( \lambda_v \nabla T_v - \sum_i h_i \vec{J}_i \right) + S_h, \quad (13)$$

$$\frac{\partial}{\partial t} (\rho_v \vec{v}_v) + \nabla \cdot (\rho_v \vec{v}_v \vec{v}_v) = -\nabla P + \nabla \cdot (\tau) + \rho_v \vec{g} + \vec{F}, \quad (14)$$

where subscript  $v$  refers to the vapor phase,  $\rho_v$  is the density ( $\text{kg}\cdot\text{m}^{-3}$ ),  $\vec{v}_v$  is the velocity ( $\text{m}\cdot\text{s}^{-1}$ ),  $S_m$  is the mass source term ( $\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$ ),  $Y_i$  is the mass fraction of species  $i$ ,  $\vec{J}_i$  is the diffusion flux of species  $i$  ( $\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ ),  $S_i$  is the species source term ( $\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$ ),  $h_v$  is the specific enthalpy of the vapor phase ( $\text{J}\cdot\text{kg}^{-1}$ ),  $\lambda_v$  is the thermal conductivity ( $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ),  $T$  represents the temperature (K),  $S_h$  is the heat source term of the vapor phase ( $\text{J}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$ ),  $P$  is the static pressure (Pa),  $\tau$  is the stress tensor (Pa) and  $\vec{F}$  represents the interfacial momentum source term ( $\text{Pa}\cdot\text{m}^{-1}$ ).

The governing equations of the liquid phase (Lagrangian phase) are:

$$\frac{d\vec{v}_l}{dt} = F_D (\vec{v}_v - \vec{v}_l) + \frac{\vec{g} (\rho_l - \rho_v)}{\rho_l}, \quad (15)$$

$$m_l C_{p_l} \frac{dT_l}{dt} = h A_l (T_v - T_l) + \sum \frac{dm_{p,i}}{dt} L_i, \quad (16)$$

where the subscript  $l$  refers to the liquid phase,  $F_D$  is related with the drag coefficient,  $Re$  represent the Reynolds number,  $\rho_l$  is the density ( $\text{kg}\cdot\text{m}^{-3}$ ),  $C_{p_l}$  is the specific heat of liquid phase ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ),  $h$  represents the convective heat transfer coefficient ( $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ ) and the last term on the right-hand side of the Equation 16 is the source term of the energy conservation

equation, given by Equation 9. The convective mass and heat transfer coefficients were calculated using the Ranz-Marshall correlation (Ranz and Marshall, 1952). Moreover, both phases were considered ideal and vapor-liquid equilibrium was estimated with Raoult's law.

The solution was obtained in steady state and the fluid flow was laminar, thus, no turbulent model was used. Numerical domain consisted in a pseudo-1D geometry with 50 m length and 0.05 m height. The discretization consisted of elements with 12.5 mm, uniformly distributed in the axial and radial directions, as shown in Figure 1.

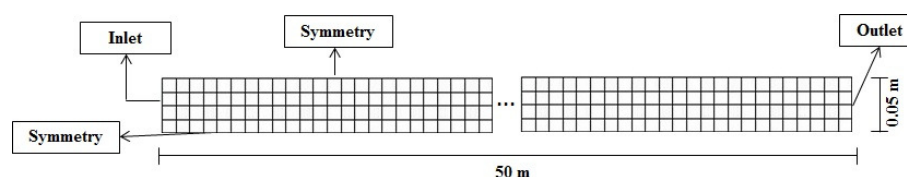


Figure 1 – Scheme of the computational domain and the numerical discretization.

Mass flow rate and pressure boundary conditions were assigned at the inlet and outlet, respectively, while symmetry was applied to the lateral boundaries, which allowed to neglect wall effects on the fluid flow. The inlet boundary conditions applied in the CFD simulations are presented in Table 1.

Table 1– Boundary conditions applied in the CFD simulations

Species	Mass fraction		T (K)		$\dot{m}$ (kg.s <sup>-1</sup> )		$d_p$ (m)	$v_l$ (m.s <sup>-1</sup> )
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor		
Methane	0.0	0.25						
n-Pentane	0.0	0.25	313.15	423.15	1.00	1.00	$5 \times 10^{-5}$	0.03
n-Hexane	0.5	0.25						
n-Octane	0.5	0.25						

The maximum deviations ( $\varepsilon$ ) of each correlation were calculated considering as reference the predictions of FSG (Equation 17), which is cited in literature as the best correlation to estimate the binary diffusion coefficients in vapor phase.

$$\varepsilon (\%) = 100 \frac{\phi - \phi_{FSG}}{\phi_{FSG}} \quad (17)$$

where  $\phi$  is the value of  $D^o$  estimated with Equations 4–7 and  $\phi_{FSG}$  is the value of  $D^o$  estimated with the FSG correlation. The convergence criteria adopted in the solution of the vapor phase were  $10^{-4}$  for continuity equation and momentum conservation equation,  $10^{-6}$  to the energy conservation equation and  $10^{-3}$  to the species conservation equation. For the liquid phase, the convergence criteria were  $10^{-5}$  to all the conservation equations.

## 4. RESULTS AND DISCUSSION

Figure 2 shows the temperature profile of liquid and vapor phases according to the correlations used to calculate the diffusion coefficients in finite concentrations,  $D^o$ . It is possible to notice that slight deviations occurred between HEA prediction and FSG prediction in the temperature of both phases, remarkable until the length of 20 m. However, they were not significant, since the maximum deviations were of 0.324 % to the vapor phase and 0.197 % to the liquid phase.

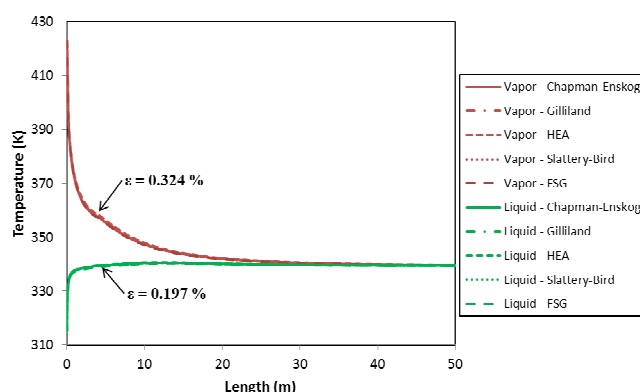


Figure 2 – Temperature profiles as a function of the correlations.

Figures 3 and 4 present the composition profiles of the liquid and vapor phases, respectively. In the liquid phase, quite small deviations were observed in the concentration profiles of n-hexane and n-octane between HEA and FSG prediction (0.757 % for n-hexane and 0.415 % for n-octane) in the first 20 m of the domain. In the vapor phase, small deviations were observed in the concentration profiles of methane and n-pentane also related to HEA correlation. The remain correlations did not present deviations related to predictions of FSG for these two components. For n-hexane and n-octane, besides HEA correlation, deviations were also observed with the predictions of Gilliland, Chapman-Enskog and Slattery-Bird associated with the prediction of FSG. Table 2 presents the percentage deviations occurred in the concentration profiles of the vapor phase components related to FSG prediction.

Table 2 – Percentage deviations of Gilliland, HEA, Chapman-Enskog and Slattery-Bird related with the prediction of FSG for the vapor phase components

Correlation	Vapor Phase $\varepsilon$ (%)			
	Methane	n-Pentane	n-Hexane	n-Octane
Gilliland	-	-	2.300	1.985
HEA	1.565	2.786	4.256	3.831
Chapman-Enskog and Slattery-Bird	-	-	0.423	0.423

It is observed that the deviations between the predictions of the correlations used are quite small and, thus, it can be concluded that the use of any of these correlations would be satisfactory to estimate  $D^o$  in this particular mixture. It should be noted that the correlations

studied are valid for nonpolar gases and systems at low pressure. Changing these conditions would imply the use of other correlations.

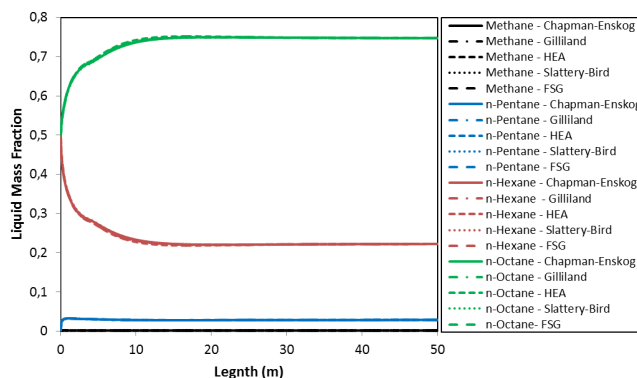


Figure 3 – Liquid phase composition profiles obtained with the different correlations.

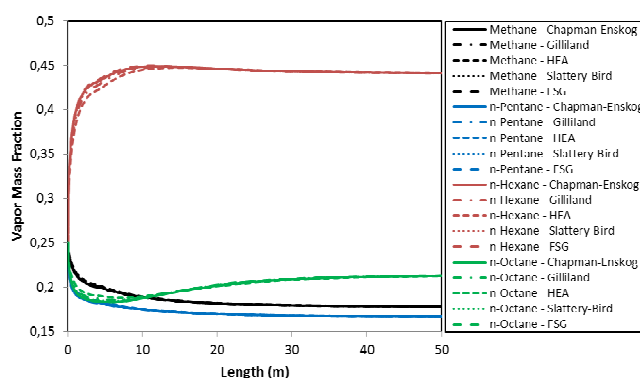


Figure 4 – Vapor phase composition profiles obtained with the different correlations.

Considering these results, the choice of correlations for the estimation of diffusion coefficients should be done considering also factors such as ease of use and availability of data to obtain its parameters. The dependence with complex parameters, as collision diameter and collision integral presented in the theoretical equation of Chapman-Enskog, that would at first improve the precision of the correlation, in most of the cases involves extensive data for their determination, which ultimately increases the uncertainty. This justify the use of simpler correlations such as FSG correlation, cited in the literature as the most accurate among the existing correlations to predict diffusivity in vapor phase (Fuller *et al.*, 1966; Huang *et al.*, 1972; Eslamloueyan and Khademi, 2010). However, in cases involving components which do not have a defined molecular structure, the use of FSG correlation would be limited and the correlations of Huang *et al.* (1972) and Gilliland (1934) may be employed in these situations.

## 5. CONCLUSIONS

The diffusion coefficients are important parameters in the determination of interfacial fluxes in multiphase flows, observed in various industrial processes. Thus, accurate evaluation



of these parameters is crucial for the correct quantification of the mass transfer phenomena. In this work, different correlations were used to calculate the diffusion coefficients at finite concentrations and the results revealed that the correlations estimated this parameter with similar accuracy. Most of deviations were associated with HEA correlation; however these deviations were relatively small. Therefore, any of the tested correlations could be used to predict the diffusion coefficient in finite concentrations in this ideal multicomponent mixture. According to the complexity of the correlations, it was noted that simple correlations become more attractive because they involve less uncertainty in their results.

## 6. ACKNOWLEDGEMENTS

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