Gas-Liquid Interface Displacement: Numerical and experimental comparative analysis for carbon dioxide diffusion into n-decane

DAMELYS ZABALA*, AURA L. LÓPEZ DE RAMOS**

*CIMEC, Escuela de Ingeniería Mecánica, **Departamento de Termodinámica y Fenómenos de

Transferencia

*Universidad de Carabobo, **Universidad Simón Bolívar * Av. Universidad, Edf. Facultad de Ingeniería, Bárbula, Estado Carabobo, **Apartado Postal 89.000, Caracas

VENEZUELA

Abstract: - A moving boundary problem was numerically solved for carbon dioxide diffusing through a n-decane liquid phase inside a glass capillary tube. The model consisted of three coupled partial derivative differential equations for mass transfer inside and between the phases. The technique for solving the model was the recent methodology developed by Illingworth and Golosnoy^[1] which allowed solute conservation and transformed the moving boundaries in fixed ones, for a diffusion process with no convective effects inside the phases. For the experimental setup, a vertical glass capillary tube was partially filled with the hydrocarbon through the lower extreme which was sealed afterward. The carbon dioxide was injected through the upper side at approximately 23.5 °C and 1480 kPa (abs). The capillary was inside a glass visualization cell filled with glycerol (same glass refractive index) to avoid image distortion by light diffraction. The gas-liquid interface displacement was recorded with a camcorder during 90 minutes. Image processing allowed determining experimental interface position for further comparison with the model prediction. This work used a different boundary condition in the gas phase, respect to the mentioned authorwork; in addition, different phase densities were considered in the interface equation. Results showed that the experimental interface position was well represented by the numerical model for cylindrical capillary tubes, whereas for square capillary tubes there was a considerable deviation between theoretical and experimental results, attributable to convective flow patterns in the square tube corners, which were not considered in the mass transfer model.

Key-Words: - Diffusion, Moving Interface, Carbon Dioxide, Numerical Modeling.

1 Introduction

Carbon dioxide diffusion in liquid hydrocarbons have been studied by many authors because of its application in enhanced oil recovery^[2-8]. In this work, diffusion experiments with a moving interface between two continuous phases (gas→liquid) are performed inside round and square glass capillary tubes, which represent a geometrical configuration without and with corners, respectively. Comparison between the interface position experimental results and the theoretical results, predicted by a movingboundary model for one-dimensional mass transfer without convective effects, were done in order to find evidence of the induced flow patterns when the corners are present.

2 Problem Formulation

2.1 Mathematical Model

For carbon dioxide, one-dimensional continuity equations for liquid and gas phases are:^[1,9]

$$\frac{\partial x_C}{\partial t} = \frac{\partial}{\partial z} \left(D_L \frac{\partial x_C}{\partial z} \right) \quad , 0 \le z \le s(t) \tag{1}$$
$$\frac{\partial y_C}{\partial t} = \frac{\partial}{\partial z} \left(D_G \frac{\partial y_C}{\partial z} \right) \quad , s(t) \le z \le L \tag{2}$$

Equations (1) and (2) are for mass transfer proces Formatted: constant phase densities, without bot Deleted: (2) with convective effects and chemical reaction. The initia Formatted: and boundary conditions are in Table 1. Making mass balance for carbon dioxide across the movin interface, its position can be determined by solvin the ordinary differential equation (3).^[1,10, 11]

$$C_{L}D_{L}\frac{\partial x_{C}}{\partial z}\Big|_{z=s(t)^{-}} - C_{G}D_{G}\frac{\partial y_{C}}{\partial z}\Big|_{z=s(t)^{+}} = \left(y_{C}^{sat}C_{G} - x_{C}^{sat}C_{L}\right)\frac{ds(t)}{dt}, \quad z=s(t)$$

Following a recent developed methodology^[1] moving boundaries are transformed in fixed ones, b definition of new spatial variables *u* and *v*.

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$$u = \frac{z}{s(t)}, \quad v = \frac{z - s(t)}{L - s(t)}$$

Table 1. Initial and border conditions

Gas phase	Liquid phase	
$t=0, \qquad y_C=y_C^{ini}$	$t=0, \qquad x_C=x_C^{ini}$	
$z = s(t), y_C = y_C^{sat}$	$z = s(t), x_C = x_C^{sat}$	
$z = L, \qquad y_C = y_C^{ini}$	$z=0, \qquad \frac{\partial_{x_C}}{\partial z}=0$	

The concentrations are defined by new dependant variables *p* and *q*.

$$p(u,t) = x_C(z,t), \quad q(v,t) = y_C(z,t)$$

The transformed equations inside the phases are (4)and (5), and their respective transformed initial and boundary conditions are in Table 2.

$$\frac{\partial p}{\partial t} - \mathscr{S}_{s}^{u} \frac{\partial p}{\partial u} = \frac{\partial}{\partial u} \left(\frac{D_{L}}{s^{2}} \frac{\partial p}{\partial u} \right) \quad , 0 \le u \le 1$$
(4)

$$\frac{\partial q}{\partial t} - \mathcal{S} \frac{1-\nu}{L-s} \frac{\partial q}{\partial \nu} = \frac{\partial}{\partial \nu} \left(\frac{D_G}{\left(L-s\right)^2} \frac{\partial q}{\partial \nu} \right), \ 0 \le \nu \le 1$$
(5)

Table 2. Transformed initial and border conditions

Gas phase	Liquid phase	
$t=0, q=y_C^{ini}$	$t=0, p=x_C^{ini}$	
$v=0, q=y_C^{sat}$	$u=1, p=x_C^{sat}$	
$v = 1, q = y_C^{ini}$	$u = 0, \frac{\partial p}{\partial u} = 0$	

The transformed interface equation is:

$$C_{L} \frac{D_{L}}{s} \frac{\partial p}{\partial u} \Big|_{u=1} - C_{G} \frac{D_{G}}{L-s} \frac{\partial q}{\partial v} \Big|_{v=0} =$$

$$\left(y_{C}^{sat} C_{G} - x_{C}^{sat} C_{L} \right) \frac{ds(t)}{dt}, \qquad u = 1, \ v = 0$$
(6)

The interface equation (6) is converted to an expression which conserves solute^[1].

$$\frac{\partial}{\partial t}\left\{s(t)C_{L}\int_{0}^{1}p(u,t)du + \left(L-s(t)\right)C_{G}\int_{0}^{1}q(v,t)dv\right\} = 0 \qquad (7)$$

The limitation for this mathematical model is that it does not consider the real shape of the interface, which forms a meniscus inside the small glass capillaries as it can be observed in Fig.4 and 5. Figure 1 shows a scheme of the mass transfer process with a flat interface.



Fig. 1. Mass transfer process illustration.

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2.2 Experimental Equipment

A visualization cell is built, with two plexiglass car (2 cm thickness) and four common glass walls ($5 c_{i}$ thickness) the joints are sealed with silicon. A scal for interface displacement measurement is marked b the capillary tube surface, before the tube is p_{1} **Deleted:** (5) inside the cell. The space between marks is 5 mm Formatted: The capillary tube is fixed to brass connectors upper and lower extremes of the cell using epoxi glue (Fig.2). The space between the capillary and th cell walls is filled with glycerol (99.5%) which has the same refractive index than the glass, to avoi distortion by light diffraction.



Fig.2. Visualization cell

The cell is joined to a metallic base by, at least, two long screws passed through to aligned holes in both plexiglass caps. The screws are supported to the caps by washers and nuts. The distance from the lowest mark and the lower extreme of the tube is recorded as well as the capillary tube length. The cell assembly is on a pneumatic vibration isolated table to minimize movement in the system. In the capillary lower extreme, a membrane is put between the tube and the brass connector to seal this side during the test. Before the test, system leaks are checked, flowing carbon dioxide at the test pressure for at least five minutes. If there are no leaks, system returns to atmospheric pressure and then the hydrocarbon (n-C10: n-Decane) is injected by this extreme, passing a syringe through a small hole in the connector and penetrating the membrane. After n-C10 injection, the syringe is removed. System vacuum is generated during five minutes and, after that, the carbon dioxide is injected through the upper side at 23.5 °C and 1480 kPa (abs) and the recording process begins. The test temperature is the environment temperature, which is controlled by an air conditioning unit. The CO_2 is supplied through a high pressure cylinder, using a pressure regulator for pressure control. The camcorder is a Sony mini DV, model DCR-HC42 (12X digital zoom) with a 12X macro lens. The camcorder is positioned in a way that the meniscus position can be observed between the marks on the capillary, as is shown in Fig. 3 y 4. In this way, it is possible to have the calibration pixel/mm direct from the test images and it is not necessary remove the cell after finishing the test to record a calibration pattern. Also, the interface initial position s(0), respect the reference axis (the capillary lower extreme) can be determined.

3 **Problem Solution** 3.1 **Mathematical Model Results**

Diffusion coefficients are considered variable in liquid phase and constant in gas phase. D_L is estimated by Caldwell and Babb^[12] equation using Scheibel correlation^[13] for dilute solution CO_2 diffusion coefficient.

$$D_{L} = \left[p D_{H}^{dil} + (1-p) D_{C}^{dil} \right] \left[1 + p \frac{\partial \ln \gamma_{C}}{\partial p} \right]$$
(8)

The term for the dilute solution n-C10 diffusion coefficient was neglected. The thermodynamic factor is calculated using activity coefficient estimated by Margules with two subscripts^[14].

$$D_{L} = (1-p) D_{C}^{dil} \left[1 - p \frac{2A}{RT} (1-p) \right]$$
(9)

The parameter A is calculated from the infinite diluted activity coefficient, γ_C^{∞} , for a temperature range from 22 to 25 °C. Average value is shown in Table 3.

$$A = RT \ln(\gamma_C^{\infty}) \tag{10}$$

$$\gamma_C^{\infty} = \lim_{P \to P_H^{sat}} \gamma_C \tag{11}$$

$$\gamma_C = \frac{\hat{\phi}_C^V P K_C}{f_C^L} \tag{12}$$

 D_G is calculated by Wilke and Lee correlation^[15]. C_G is aproximated to pure CO₂ molar density which it is calculated by Pitzer and Sterner equation of state^[16]

Table 3. Data at P=1480 kPa (abs), T=23.5 °C					
	sat	0.9994	D _G	$2.125.10^3$	
	y_{C}	[17]	$[\text{mm}^2/\text{h}]$		
	ini	1	А	7900	
	y_{C}		[kJ/kmol]		
	sat	0.1884	C _G	0.651.10 ⁻⁶	
	X_C	[17]	[mol/mm ³]		
	ini	0	C _L (adjusted)	2.19. 10 ⁻⁶	
	\mathcal{X}_{C}		[mol/mm ³]		

C_L is initially estimated as the pure n-decane molar density at test temperature and pressure. The final value is determined by adjusting the model results with the cylindrical capillary tube results and C_L is lower than the initial value as it is expected because the carbon dioxide diffusing into the liquid n-decane reduces liquid density.

Table 4. Capillary tube data				
Capillary	Cylindrical	Square		
L[mm]	194	210		
ID	Diameter	Side		
[mm]	2	2		
Material	Borosilicate	Quartz		

The partial derivative equation system (4), (5) and (2)is discretized and numerically solved by finit difference method, using Mathcad® 2001 algorithms used are of first order accuracy. The space discretisation is done with a fixed mesh for gas phase and with three different step sizes for liquid phas the smallest one near the interface. The timestep size is fixed and the finite difference solution scheme semi-implicit, because the concentration term present in the coefficient diffusion in the liquid phas are evaluated in the previous time in order to have othe constant coefficient matrix. All the concentration terms are evaluated in the present time. In order to compare numerical model stability two different timesteps are used. The timestep size are: $10^{-2}/3$ and $10^{-3}/3$ hours. The reason for selectin divisor numbers multiple of three is to compar experimental and theoretical results in the same tim Formatted:

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Fig.3 Model results for two timestep sizes

3.2 Experimental Results

After recording the diffusion process, the images are processed to determine the interface position relative to reference axis. Figures 4 and 5 show some examples of these images.



a)t=0 b)t=60 min Fig.4. Displacement inside cylindrical capillary



a)t=0 b)t=60 min Fig.5. Displacement inside square capillary



Fig.6. Experimental and theorical results comparison

The experimental results for interface displacement relative to its initial position are compared with the results predicted by the mathematical model as it is shown in Fig. 6. Interface displacement for square capillaries is larger than the displacement for cylindrical ones. This behavior is similar to the reported by other authors, in experiments done at different temperature and pressure and with other saturated hydrocarbons^[5-8].

Also, Fig. 6 shows the model result properly represents the interface displacement inside the cylindrical capillary. The model curve slope is almost constant and this can be product of the algorithm first order accuracy. The average relative error between the model and the cylindrical results is 5.6%. On the other hand, square capillary result presents a considerable deviation (38.2%) from those predicted by the model.

4 Conclusion

A mass transfer model which considers nonconvective effects, constant phase densities and variable diffusion coefficient in liquid phase is appropriate to represent CO_2 diffusion process in liquid n-C10, inside a cylindrical capillary tube, in the test time interval.

Modeling of the diffusion process inside square capillary tubes may require the continuity equation convective term be considered, at least in the liquid phase, where the presence of liquid filaments in the tube corners can be responsible for enhanced mass transfer.

List of Symbols

 C_j = molar density of "j" phase, [mol/mm³]. dt = timestep size, [h]

 $D_i = CO_2$ diffusion coefficient in "j" phase, [mm²/h].

 D_C^{dil} = dilute solution CO₂ diffusion coefficient, [mm²/h].

 D_{H}^{dil} = dilute solution n-C10 diffusion coefficient, [mm²/h].

 f_C^L = pure liquid CO₂ fugacity, [kPa] ID= inner dimension, [mm] Kc= CO₂ equilibrium ratio

L= capillary tube lenght, [mm].

P= absolute pressure, [kPa]

 P_{H}^{sat} = saturation pressure, [kPa]

R= 8.3144 kJ/kmol K

s=s(t)= interface position, relative to capillary tube bottom [mm].

 $s = \frac{ds(t)}{dt}$ = interface velocity,[mm/h].

T= temperature, [K]

 $x_{C} = CO_2$ molar fraction in liquid phase, [-].

 y_{C} = CO₂ molar fraction in gas phase, [-].

Greek letters

 $\hat{\phi}_{C}^{V} = CO_{2}$ fugacity coefficient in gas mixture, [-]

Subscripts L= liquid phase G= gas phase

Superscripts ini= initial sat= saturation

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References:

- Illingworth, T.C.; Golosnoy, I.O. Numerical solutions of diffusion-controlled moving boundary problems which conserve solute. *Journal of Computational Physics*, Vol.209, N1, 2005, pp. 207-225.
- [2] Grogan, A.; Pinczewski, V. The role of molecular diffusion processes in tertiary carbon dioxide flooding. Paper SPE/DOE 12706, presented at SPE/DOE Fourth Joint Symposium on Enhanced Oil Recovery, Tulsa, OK, Apr. 15-18, 1984.
- [3] Campbell, B.; Orr, F. Flow visualization for CO₂/crude oil displacements. *Society of Petroleum Engineers Journal*, 1985, pp.665-678.
- [4] Grogan, A.; Pinczewski, V.; Ruskauff, G.; Orr, F. "Diffusion of carbon dioxide at reservoir

conditions: Models and Measurements". Paper SPE/DOE 14897, presented at SPE/DOE Fifth Symposium on Enhanced Oil Recovery, Tulsa, OK, Apr. 20-23, 1986

- [5] Aguilera, M.E.; Cerro, R.L and López de Ramos,
 A. Enhanced CO₂ diffusion in wedges. Chem. Eng. J. Vol. 87, 2002, pp. 31-40.
- [6] López de Ramos, A. Capillary enhanced diffusion of CO₂ in porous media. Ph.D. Dissertation, University of Tulsa, 1993.
- [7] Garrido, A. Estudio Teórico Experimental de la Transferencia de Masa en Líquidos Confinados en Regiones con Angularidades. M.Sc Thesis, Universidad Simón Bolívar, 2005.
- [8] De Freitas, A. Estudio del efecto de las esquinas en la transferencia de masa en medios porosos.
 M.Sc Thesis, Universidad Simón Bolívar, 2005.
- [9] Bejan A. Heat Transfer. John Wiley & Sons, 1995.
- [10] Unlusu, Betul; Sunol, Aydin K. Modeling of equilibration times at high pressure for multicomponent vapor-liquid diffusional processes. *Fluid Phase Equilibria*. Vol. 226, 2004, pp. 15-25.
- [11] Sassi, M.; Raynaud, M. Solution of the movingboundaries problems. *Numerical Heat Transfer Part B*, Vol.34, 1998, pp.271-286.
- [12] Caldwell C.S.; Babb, A.L. Diffusion in ideal binary liquid mixtures. J. Phys. Chem. Vol. 60, 1956, pp 51-56.
- [13] Scheibel, E.G. Ind.Eng.Chem. Vol.46, 1954, pp. 2007.
- [14] Prausnitz, J.; Lichtenthaler, R. y Gomes, E. "Termodinámica Molecular de los Equilibrios de Fases". Prentice Hall, 2000.
- [15] Wilke, C.; Lee. Ind.Eng.Chem. Vol.47, 1955, pp.1253.
- [16] Pitzer, K.S.; Sterner, S.M. Equations of state valid continuously from zero to extreme pressures for H₂O and CO₂. *J.Chem.Phys.* Vol. 101 (4), 1994, pp. 3111-3116.
- [17] Reamer, H.; Sage, B. Phase equilibria in hydrocarbon systems. Volumetric and phase behavior of the n-decane-CO₂ system. *J.Chem.Eng.Data.* Vol. 8, 1963, pp. 508-513.