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Study of thermodiffusion of carbon dioxide in binary mixtures of n-butane & carbon dioxide and n-dodecane & carbon dioxide in porous media

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ABSTRACT

Convection due to a thermodiffusion phenomenon has an important effect on component separation of hydrocarbon mixtures in a porous medium. A numerical study of carbon dioxide diffusion in porous medium is investigated in the presence of different fluid mixtures such as n-butane & carbon dioxide and n-dodecane & carbon dioxide single phase. In this paper, all physical properties with an exception of the mixture conductivity are assumed as varying with temperature and concentration. The fluid is maintained at a pressure of 150 bar and remains in the liquid state. Constant temperature gradients in horizontal and vertical directions are applied on the three-dimensional porous domain. Thermodiffusion coefficients applied in simulation were calculated by using Abbasi et al.'s [J. Non-Equilib. Thermodyn. 35 (2010) 1] thermodiffusion model. Results reveal that for a certain concentration of carbon dioxide, the thermodiffusion coefficient reaches a maximum leading to large separation. In the presence of the Soret effect, the vertical density distribution tends closer to the one without the Soret effect. With an increase in the permeability, the convection becomes dominant and contributes to a decrease in the vertical and horizontal component separation considerably.

1. Introduction

Thermodiffusion as well as molecular diffusion is one way in mass flux in multicomponent systems in which is driven by temperature gradients. Thermodiffusion along the effect of natural convection has a great effect in concentration distribution in hydrocarbon reservoirs, and it can either lessen or weaken the separation in mixtures. A variety of researches have studied the effect of thermodiffusion in porous medium [1–3]. It was found that convection has an important role on the accuracy of Soret measurement. Costeseque et al. [4] carried out diffusion experiments in both free and porous medium Soret cells. It was found that the molecular diffusion and thermodiffusion coefficients in porous medium were related to those ones in clear fluid via the tortuosity. However, the ratio of the molecular diffusion coefficient to the thermodiffusion coefficient, known as Soret coefficient for binary mixtures, is identical for both configurations. Riley and Firoozabadi [5] presented a model to investigate the effects of natural convection and thermodiffusion along with molecular and pressure diffusions on a single-phase binary hydrocarbon mixture in a horizontal cross-sectional reservoir in the presence of a prescribed linear temperature field. It was found that the permeability has a great effect on the horizontal compositional variation. Delware et al. [6] studied these phenomena for a binary system in a square cavity. Their results showed that in the lateral heating case, the Soret effect is found to be weak; whereas in the bottom heating case the Soret effect is more prominent. Nasrabadi et al. [7] presented a numerical simulation of two-phase muticomponent diffusion and natural convection in porous medium. Thermodiffusion, pressure diffusion, and molecular diffusion were included in the diffusion expression from the thermodynamics of irreversible process. Results showed that the natural convection has an important role on the phase distribution in the gas and oil non-isothermal medium. Jaber et al. [8] simulated Soret effect for a ternary mixture in porous cavity considering variable viscosity and diffusion coefficients. It was found that for a permeability below 200 md, the thermodiffusion has a dominant effect; and above this level, buoyancy convection becomes the dominant mechanism. In addition, it was noted that the variation of viscosity has an important effect on the molecular and thermodiffusion.

Among different thermodiffusion models [9–20], the kinetic theory and non-equilibrium thermodynamics have more reliable results. In the kinetic approach, thermodiffusion coefficients are considered in terms of the specific heat of transport of the two

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components in a binary mixture. The net heat of transport was described as the amount of energy which must be absorbed by the region per mole of the component diffusing out so as to keep the steadiness of the temperature and pressure of the mixture [21]. Dougherty and Drickamer [13,14] developed a kinetics model for the net heat of transport in a binary mixture. In their model, the proposed activation energy by Eyring viscosity theory was used in estimating the net heat of transport. Shukla and Firoozabadi [15] proposed a model for the net heat of transport in a binary mixture. Their kinetics model was based on the Dougherty and Drickamer kinetics approach. In the Shukla and Firoozabadi model, the evaporation energy is four times bigger than the activation energy. Both Dougherty & Drickamer and Shukla & Firoozabadi models demonstrated good starting in the calculation of the net heat of transport, but they did not satisfy completely the thermodiffusion estimation [13–15,18]. Abbasi et al. [19,20] modified the Dougherty & Drickamer and Shukla & Firoozabadi models in the calculation of the net heat of transport. They proposed two new theoretical models for estimation of the activation energy in hydrocarbon mixtures based on the free volume theory. In their models [19,20], molecular size effect has an important role in the estimation of the activation energy of each component in a mixture. Their proposed models have been applied to predict binary thermodiffusion coefficients of several mixtures of linear chain and aromatic hydrocarbons in different compositions and temperature. The result showed that proposed models provides a significant improvement in the accuracy of thermodiffusion modeling for the hydrocarbon binary mixtures.

Tertiary oil recovery consists some operations that are in general done towards the end of life of an oilfield, to maintain oil production. In tertiary oil recovery the flow properties of crude oil and the rock–fluid interactions in the reservoir will modify to improve oil flow. One of the techniques in tertiary displacements of reservoir crude oil is CO_2-injection [22]. In developing the numerical simulation technique for miscible displacement in porous media, one can expect that molecular diffusion and thermodiffusions of CO_2 could play an important role in determining the concentration distribution. The main objective of this work is to investigate the effect of the temperature variation along with Soret effect in concentration distributions in a porous medium. In this present work, the thermodiffusion convection of a single-phase binary mixture of n-butane & carbon dioxide, and n-dodecane & carbon dioxide at a pressure of 150 bar in a porous medium is presented. In this study, the molecular diffusion and the thermodiffusion model are presented in Section 2, mathematical model in porous medium is presented in Section 3, system setup and simulation parameters are presented Section 4, and the consequences of the thermodiffusion convection are discussed in the Numerical results section.

2. Molecular diffusion and thermodiffusion model

The Maxwell–Stefan diffusion coefficient, $\tilde{D}_{ij}$, can be calculated from the binary infinite dilution diffusion coefficient. Taylor and Krishna [23] suggested the following formula for binary mixtures:

$$\tilde{D}_{ij} = \left(D_{ij}^0\right)^{x_j}\left(D_{ji}^0\right)^{x_i}\prod_{\substack{k=1\\k\neq i,j}}^{2}\left(D_{ik}^0 D_{jk}^0\right)^{x_k/2} \tag{1}$$

where D_{ij}^0 is the molecular diffusion coefficient of i component infinitely diluted in a binary mixture and x_i is the mole fraction of component i. According to the theory of mass transfer, The Fick molecular diffusion D can be expressed by $\tilde{D}_{ij}$ as follows:

$$D = B^{-1}\Gamma \tag{2}$$

where B and Γ are matrices, which are defined with the following formula:

$$\begin{aligned} B_{ij} &= -x_i\left(\frac{1}{\tilde{D}_{ij}}-\frac{1}{\tilde{D}_{i2}}\right), \quad i\neq j\\ B_{ij} &= \sum_{\substack{k=1\\k\neq i}}^{2}\frac{x_k}{\tilde{D}_{ik}}+\frac{x_i}{\tilde{D}_{i2}}, \quad i=j\\ \Gamma_{ij} &= x_i\frac{1}{f_i}\frac{\partial f_i}{\partial x_j} \end{aligned} \tag{3}$$

where f_i is the fugacity of component i.

The expression given by Hayduk–Minhas [23] is used in this study to calculate the diffusion coefficient in dilute binary mixture.

$$D_{ij}^0 = 13.3\times10^{-8}V_{nor,i}^{-0.71}\eta_j^{(10.2/V_1-0.791)}T^{1.47} \tag{4}$$

here $V_{nor,i}$ is the molar volume of component i at its normal boiling point, η_j is the viscosity of pure component j, and T is the temperature.

On the basis of the frame of non-equilibrium thermodynamics thermal diffusion coefficients in a multicomponent mixture can be calculated as follows:

$$D_i^T = \sum_{k=1}^{N-1}L_{ik}\left(\frac{Q_k^*}{M_k}-\frac{Q_N^*}{M_N}\right)\frac{1}{T^2} \tag{5}$$

L_{ik} is the corresponding phenomenological Onsager coefficient [24]. Q_k^* is the net heat of transport of k-comp in the mixture. The net heat of transport is the main challenge in thermodiffusion.

Shukla and Firoozabadi [15] proposed a model based on the kinetic theory by Dougherty and Drickamer [13,14] as follows.

$$Q_k^* = -\frac{\overline{U}_k}{\tau_k}+\sum_{k}^{2}\frac{x_k\overline{U}_k}{\tau_k}\frac{V_k}{\sum_{k}^{2}x_kV_k} \tag{6}$$

Abbasi et al. [20] proposed a model based on free volume theory as follows.

$$\begin{aligned} Q_k^* = &-\frac{\overline{U}_k}{\left(\frac{\sum_{k=1}^{2}x_kV_k}{V_k}\frac{\sum_{k=1}^{2}x_kM_k}{M_k}\right)^{0.5}\tau_{pure,k}}\\ &+\sum_{k}^{2}\frac{x_k\overline{U}_k}{\left(\frac{\sum_{k=1}^{2}x_kV_k}{V_k}\frac{\sum_{k=1}^{2}x_kM_k}{M_k}\right)^{0.5}\tau_{pure,k}}\frac{V_k}{\sum_{k}^{2}x_kV_k} \end{aligned} \tag{7}$$

Eq. (7) is the modified equation of Shukla and Firoozabadi model [15] in estimation the net heat of transport. $\tau_{pure,k}$ is the ratio of the evaporation energy to the activation energy in pure limits, $\overline{U}_k$ is partial molar internal energy, V_k is the partial molar volume, and M_k is the molecular weight of component k. The ratio of the evaporation energy to the activation energy in pure limits, $\tau_{pure,k}$, may be calculated based on Eyring viscosity theory as follows [25]:

$$\tau_{pure,k} = \frac{\overline{U}_k}{RT^2\left(\frac{\partial\ln\eta_k}{\partial T}\right)} \tag{8}$$

Thermodiffusion coefficient estimation based on free volume theory has been found to be most reliable and represents