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The Impact of Gravity and Molecular Diffusion on the Compositional gradient in Gas Reservoirs

By

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A report submitted in partial fulfillment of the requirements for the MSc and/or the DIC.

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DECLARATION OF OWN WORK

I declare that this thesis '**The Impact of gravity and Molecular Diffusion on the Composition Gradient in Gas Reservoirs**' is entirely my own work and that where any material could be construed as the work of others, it is fully cited and referenced, and/or with appropriate acknowledgement given.

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ABSTRACT

There has been an increasing interest in the petroleum industry to have a full understanding of the fluxes leading to compositional variations in hydrocarbon reservoirs, as this critically affects reservoir management and field development. The most important impacts of compositional variations are:

- Estimation of the hydrocarbon resources,
- Indication of compartmentalisation, and
- Indication of the reservoir filling history, thus the likelihood of finding more gas in the nearby structures. This is the impact investigated in this work.

Components distribution in the reservoir is mainly affected by diffusion (molecular, pressure and thermal) and natural convection.

This paper investigates the impact of gravity and molecular diffusion on the compositional gradient in the LaBarge Field. The LaBarge is a gas reservoir which is currently thought to have been filled 50 million years ago. It has an unusual composition as non-hydrocarbons make up about 80% of the total, with methane constituting the remainder. The currently observed composition profile at the field shows CH₄ varying from 23% at the crest to 5% at the gas water contact.

Using irreversible thermodynamics to model the impact of gravity and molecular diffusion on the fluid in the LaBarge field; compositional profiles were produced and compared to the currently observed profile. These two profiles do not match; leading us to believe the LaBarge was filled more recently about 4 million years ago and is still undergoing the impact of gravity and molecular diffusion.

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The Influence of Gravity and Molecular Diffusion on the Compositional Gradient In Gas Reservoirs

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Abstract

There has been an increasing interest in the petroleum industry to have a full understanding of the fluxes leading to compositional variations in hydrocarbon reservoirs, as this critically affects reservoir management and field development. Components distribution in the reservoir is mainly affected by diffusion (molecular, pressure and thermal) and natural convection.

This paper investigates the impact of gravity and molecular diffusion on the compositional gradient in the LaBarge Field. The LaBarge is a gas reservoir which is currently thought to have been filled 50 million years ago. It has an unusual composition as non-hydrocarbons make up about 80% of the total, with methane constituting the remainder. The currently observed composition profile at the field shows CH₄ varying from 23% at the crest to 5% at the gas water contact.

Using irreversible thermodynamics to model the impact of gravity and molecular diffusion on the fluid in the LaBarge field; compositional profiles were produced and compared to the currently observed profile. These two profiles do not match; leading us to believe the LaBarge was filled more recently about 4 million years ago and is still undergoing the impact of gravity and molecular diffusion.

Introduction

Understanding the movement of petroleum fluids through the pores of sedimentary rocks is of enormous commercial importance. A lot of work has been carried out on extraction of petroleum fluids; however the understanding of how these fluids travel and accumulate in the reservoir is somewhat superficial. An improved understanding of this will help to improve the planning of extraction programmes and increase the precision of petroleum exploration.

Petroleum is formed in the subsurface of fine grained source rock by the deposition of dead organisms. These dead organisms may be converted to kerogen at favourable temperatures and pressures. Kerogen is broken down to produce mobile petroleum fluid at about 100 °C. The fluid then migrates to pores of coarser and more permeable rocks where it accumulates and is then be extracted.

After migration into the trap, the segregation of crude oil and gas components of different mass densities may be caused by pressure/gravity and thermal diffusion. In many cases there is evidence of contribution of other fluxes; these fluxes mainly originate from migration (reservoir filling), leaky seals, natural convection, chemical reaction, biodegradation, water-washing, current reservoir charging, multiple reservoir charges and variation in kerogen maturation. Taking into account all these phenomena, establishing a consistent profile of fluid distribution in the reservoir is an important yet difficult task for the petroleum industry. Among all these forces, gravity has the most impact on the compositional segregation. Molecular diffusion counters the effect of the segregating forces, tending to even out the compositional gradient.

Given enough time, the distribution of the components of the petroleum fluid in the reservoir will achieve steady state. The dynamics of the steady state is usually governed by various degrees of diffusion (molecular, pressure and thermal) and natural convection. The composition variation at steady state in the reservoir is important, as it aids the location of the economic viable areas of the reservoir for exploration. Compartmentalisation in the reservoir may hamper or delay the attainment of steady state in the reservoir; as it will hamper the mixing process of molecular diffusion.

There has been an increasing interest in the oil industry to gain proper understanding of compositional variations in the hydrocarbon reservoirs. The main objective is to identify the reasons behind various significant trends in compositional variations; Metcalfe *et al.* (1988) observed a vertical variation with lighter components at the top the reservoir, Ghorayeb *et al.* (2003) found a vertical variation with decrease of heavy component with depth, horizontal composition variations have been observed by Hamoodi *et al.* (1996) and negligible composition variations have been studied by Lee and Charera (1998).

There have been several attempts made to model compositional gradient in reservoirs. The most studied case is the effect of gravity in a convection free system (Sage and Lacey (1939), Schulte (1980), Montel and Gouel (1985) and Wheaton (1991)). From these studies one mainly concludes that gravity causes the heavier component to segregate towards the bottom of the reservoir. The impact of thermal diffusion in 1-D convection free has also been studied (Shieh (1968), Holt *et al.* (1983), Whiston and Belery (1994) and Høier and Whitson (2000)). It was found that thermal diffusion generally counteracts gravity, resulting in composition gradients with are smaller than that of the predicted isothermal gravity model. The impact of convection in reservoirs has also been widely studied; Jacquim (1986) and Riley and Firoozabadi (1998) to name a few.

Recently, Galliéro and Montel (2008) derived a relationship between for steady state solution of pressure/gravity diffusion coupled with molecular diffusion. Besong (2010) developed an explicit transient solution for a system under the influence of gravity and molecular diffusion.

The purpose of this work is to analyse the impact of gravity and molecular diffusion on the LaBarge Field; which is gas reservoir located in Wyoming, USA. The LaBarge comprises of CH₄ and other non-hydrocarbons. It is currently assumed that this field was charge 50 million years ago (Ma). BP has investigated alternative filling scenarios to produce the steady state profile observed at the LaBarge field using the MPATH software. These simulations focused primarily on reservoir fill and spill combined with gravitational segregation, not taking into account the effect of pressure and molecular diffusion. The steady state profile produced from this work closest to that observed in the field comprised of a reservoir model with a spill point (the field spilling into another formation); with the reservoir originally filled with CO₂, and then charged with CH₄ for 20,000 years. However, this was obtained when the simulation was carried out only for 800,000 years. This is quite a short time scale compared to the actual time since the reservoir was filled (50 Ma). Moreover, order of magnitude calculations suggest that molecular diffusion could completely mix CO₂ and CH₄ within an order of 10 million years. However, these calculations neglect the effect of gravity (pressure) diffusion which could help to maintain the observed CH₄ distribution shown in Fig.2.

In this work we shall investigate the impact of both gravity and molecular diffusion by producing a steady state compositional profile based on these two fluxes; and then try to match this profile to that currently observed at the reservoir. This and examining the time-scales for the attainment of steady state help shed some light into how this field was charged; as this is currently not fully understood.

Methodology

Diffusion

The diffusive mechanisms that affect the distribution of components in the reservoir are:

1. Molecular diffusion
2. Pressure diffusion
3. Temperature diffusion

In hydrocarbon reservoirs, it is usually the case that pressure diffusion is very fast and molecular diffusion is relatively slow. However, pressure diffusion can become very slow across permeability barriers in reservoirs.

Molecular Diffusion

This is a process which tends to reduce and eventually eliminate the chemical potential gradients by random motions of molecular species. In the case of a freshly filled reservoir with an initially non-uniform distribution of chemical components, diffusion will cause the redistribution of molecules so that horizontal concentration gradients will be eliminated and vertical (gravitational or thermally induced) gradients become established.

The diffusion equation for a binary mixture *A* and *B* in 1-D is given by (Taylor and Krishna, 1993):

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial z} \left(C D_{AB}^M \frac{\partial x_A}{\partial z} \right) \quad (1)$$

where *c* is the concentration of the mixture, *x_A* is the mole fraction of component *A*, *D_{AB}^M* is the diffusion coefficient of *A* in *B*.

Pressure Diffusion

Pressure diffusion is a process that leads to compositional gradient governed by the pressure gradient. Where there is only hydrostatic pressure this process is referred to as gravity diffusion. Based on irreversible thermodynamics (Firoozabadi, 1999), the segregation caused by gravity for a binary mixture in an isothermal system is given by:

$$\frac{\partial C_A}{\partial t} = - \frac{\partial}{\partial z} \left(C \frac{D_{AB}^g}{RT} x_A (\rho \bar{v}_A - M_A) \right) \quad (2)$$

where \bar{v}_A is the molar volume of *A*, ρ is the mass density, *M_A* the molecular weight of *A*, *R* is the ideal gas constant and *T* is the temperature. The magnitude of gravity diffusion (segregation) is governed by the difference in density of the various components and its rate is influenced by the mobility of *A* in the medium and the acceleration due to gravity (Besong, 2010). In hydrocarbon reservoirs, because of the often considerable height of the petroleum columns, gravity diffusion significantly alters the equilibrium concentration so that they vary with depth. This result in the denser components tending to be more concentrated towards the bottom of the reservoir and vice versa.

Thermal Diffusion

The tendency of a convection-free mixture to separate under the influence of a temperature gradient is known as thermal diffusion or the Soret effect. In this process, the transport of matter takes place with thermal gradient (usually the geothermal gradient). Geothermal gradients usually result in an increase of temperature with depth. The geothermal gradient is related to the thermal conductivity of the rock body and the heat flux. Sometimes the thermal conductivity is not uniform because of the

mineralogical composition of the rock, porosity and presence of gas or water. The different thermal conductivities between adjacent lithologies can lead to a horizontal temperature gradient (which can result in thermal convection). Holt *et al.* (1983) found that the impact of thermal diffusion is of similar magnitude to that of gravity. Using irreversible thermodynamics (Firoozabadi, 1999) the impact of thermal diffusion can be derived for a binary mixture:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial}{\partial z} \left(c D_{AB} \frac{k_T}{T} \frac{\partial T}{\partial z} \right) \quad (3)$$

k_T is known as the thermal diffusion ratio.

Natural Convection

In addition to diffusion, there may be a bulk movement due to density gradients. This density gradient may be established by either concentration or thermal gradients. In contrast to diffusion, convection will completely homogenize a reservoir removing any thermally or gravitationally induced concentration gradients (W. England *et al.*, 1987). Segregation is effective only if natural convection is low enough to avoid mixing or if the filling process is slow enough. In order for natural convection to be active at reservoir scale, we have to compare the times taken for the diffusion and convection processes to attain equilibrium. Montel *et al.* (2007) stated equations for the characteristic time for molecular diffusion;

$$t_M^A = \frac{H^2}{D_A} \quad (4)$$

where t_M^i is the characteristic time for molecular diffusion, H is the height of the reservoir and D_A is the generalised diffusion coefficient of component A .

$$t_c = \frac{\mu}{\rho g k \alpha_p \nabla_z T \sin(\beta)} \quad (5)$$

where α_p is the thermal expansion coefficient of the fluid, β is the angle between the gravity vector and temperature gradient in the reservoir, $\nabla_z T$ is the temperature gradient with depth and μ is the viscosity of the fluid in the reservoir.

Montel *et al.* (2007) summarised three different scenarios for a system under the influence of diffusion and natural convection:

- $t_c \gg t_M^A$: No or very slow convection occurs.
- $t_c \ll t_M^A$: Very active convection; the homogenous fluid profile in the whole reservoir.
- $t_c \leq t_M^A$: Segregation process should be significantly increased when there is a similar timescale for natural convection and diffusion in the reservoir.

Mathematical Formulation

In this work, the impact of gravity and molecular diffusion on the LaBarge field will be investigated using the numerical solution for the separation-mixing equation; which has been implemented as a C++ code by Besong (2010). The steady state results obtained from the numerical solution were then verified using an analytic solution.

In this section, the thermodynamics behind the separation-mixing equation and the trivial aspects of the computer program are summarised.

The driving force of molecular diffusion in a non-ideal fluid d_A^M in terms of mole fraction gradients ($\nabla_z x_A$) is expressed as (Taylor and Krishna, 1993):

$$d_A^M = \frac{x_A}{RT} \nabla_{T,P} \mu_A = -\Gamma \nabla_z x_A \quad (6)$$

where Γ is the thermodynamic factor. The molecular diffusion flux can be obtained by multiplying d_A^M by $c D_{AB}$; c is the molar concentration of the mixture and D_{AB} is the fickian diffusion coefficient.

$$J_A^M = -c D_{AB} \Gamma \nabla_z x_A \quad (\text{mol. m}^{-2} \text{s}^{-1}) \quad (7)$$

The driving force due to gravity has also been derived using irreversible thermodynamics. Firoozabadi (1999) explains how to obtain the driving force for a multi-component system. As we shall be working on a binary system, we will use the equation derived by Besong (2010). The Gibbs sedimentation expression gives:

$$d\mu_A = -M_A dz \quad (8)$$

This can also be expressed in terms of pressure and mole fractions

$$d\mu_A = \left(\frac{\partial \mu_A}{\partial P} \right)_T dP + \left(\frac{\partial \mu_A}{\partial x_A} \right)_{P,T} dx_A \quad (9)$$

and in terms of partial molar volume \bar{v}_A :

$$\left(\frac{d\mu_A}{dP}\right)_T = \bar{v}_A \quad (10)$$

Combining all three equations, we obtain:

$$\left(\frac{\partial\mu_A}{\partial x_A}\right)_{P,T} \frac{dx_A}{dz} = (\rho\bar{v}_A - M_A)g \quad (11)$$

The molar flux for gravity segregation can be obtained by multiplying eq. (11) by the mobility term $\left(\frac{D_{AB}}{RT} c x_A\right)$:

$$J_A^P = \frac{D_{AB}}{RT} c x_A \frac{\partial\mu_A}{\partial z} = \frac{D_{AB}}{RT} c x_A (\rho\bar{v}_A - M_A)g \quad (12)$$

The mass density ρ can be expressed as:

$$\rho = \frac{x_A M_A + x_B M_B}{x_A \bar{v}_A + x_B \bar{v}_B} \quad (13)$$

In a 1-D binary mixture system under the influence of gravity and molecular diffusion, with vertical concentration gradients, the molecular flux is parallel to the acceleration due to gravity. Applying conservation of mass yields:

$$\frac{\partial c_A}{\partial t} = -\frac{\partial J_A^M}{\partial z} - \frac{\partial J_A^P}{\partial z} \quad (14)$$

where ∂J_A^M is the flux of A due to concentration gradient and ∂J_A^P is the flux due to pressure difference between the components. Partially differentiating eq. (7) and (12) with respect to the reservoir position and substituting into eq.(14), we obtain:

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial z} \left(c D_{AB} \Gamma \frac{\partial x_A}{\partial z} \right) - \frac{\partial}{\partial z} \left(\frac{c D_{AB} g}{RT} x_A \left(\frac{x_A M_A + x_B M_B}{x_A \bar{v}_A + x_B \bar{v}_B} \bar{v}_A - M_A \right) \right) \quad (15)$$

This gives the separation-mixing equation for gravity and molecular diffusion.

Numerical solution

Eq. (15) has to be solved in order to obtain the mole fraction profile of the components over time. However, this cannot be done analytically; therefore a computer program was developed by Besong (2010) to solve it numerically. The numerical method provides an explicit solution to the separation-mixing equation. This utilises the finite volume method with operator splitting in a reservoir of height of $H = 2L$, with a spatial position of $-L \leq z \leq L$. At each time step, the program first solves for the mole fraction in the molecular diffusion part of eq. (15), and then uses this value to solve for the mole fraction in the gravity diffusion part. To achieve this, a boundary condition which implements zero flux at the boundaries (of the reservoir) is set for each part of the process. This is obtained by splitting the homogenous Robin boundary conditions, to be applied for each process (Besong, 2010). Therefore, at the two reservoir boundaries:

$$J_A^M + J_A^P = 0 \text{ at } z = -L \text{ and } z = L \quad (16)$$

Since the program does not incorporate sources or sinks, there will be no interchange between the molecular and gravity flux. Thus;

$$J_A^M = 0 \text{ at } z = -L \text{ and } z = L \quad (17)$$

$$J_A^P = 0 \text{ at } z = -L \text{ and } z = L \quad (18)$$

we shall now discuss the other aspects of the computer program.

Numerical Stability

Explicit numerical solutions to problems sometimes produce unrealistically large values as the simulation runs (instabilities). This is due to the use of large time steps for a given grid size. The finite volume method used has a maximum value of the ratio of the time step to the power function of the grid size. This maximum value is called the CFL (Courant-

Friendrichs-Lewy) condition (Thomas, 1995). This is the primary stability criterion we implemented in the computer program. The CFL condition for both gravity and molecular diffusion was defined by Besong (2010):

Molecular diffusion:

$$\delta t_D = \frac{(\delta z)^2}{2\Gamma D_{max}} \quad (19)$$

where δt_D is the maximum stable time step for molecular diffusion, δz is the grid size and D_{max} is the largest absolute value of the diffusion coefficient.

Gravity diffusion:

$$\delta t_P = \frac{\delta z}{A_{max}} \quad (20)$$

where δt_P is the stability limit for the time step for gravity diffusion and A_{max} is the largest value of $\frac{1}{RT} D \frac{\partial \left(\frac{x_i(\rho v_i - M_i)g}{RT} \right)}{\partial x_i}$ for the two components of the binary mixture among all spatial points of the current time step. The time step utilised in the numerical method is the minimum of the two. $\delta t = \min(\delta t_D, \delta t_P)$.

Equilibrium Criteria and Grid Refinement

Besong (2010) defined the maximum possible percentage difference in the mole fraction that indicates the point the system reaches equilibrium to be $2.5 \times 10^{-5}\%$. This was used as the stopping criteria for the simulations run for the LaBarge field using the computer program. The minimum grid size that will yield accurate results for the numerical method was also found by Besong (2010) to be 21. These two parameters were chosen and were used in our simulations, as they give accurate results whilst minimising the computational effort.

Mass Conservation

In the numerical method, mass conservation is implemented in the whole closed reservoir, to verify that no material is lost or gained from the start of the simulation till the system reaches steady state.

Diffusion Coefficient in Porous Media

The equations presented so far for molecular and gravity diffusion has been derived for a mixture in free space. However, a reservoir is a porous medium and diffusion is reduced as molecules cannot travel freely; rock grains obstruct their path. The effective diffusion coefficient in a saturated porous medium is given by (Saripalli *et al.*, 2002):

$$D = \frac{D_f \beta \phi}{\lambda} \quad (21)$$

where D_f is the diffusivity in a free space, $0 \leq \beta \leq 1$ is the constriction factor, $0 \leq \phi \leq 1$ is the effective porosity and λ is the tortuosity. The multiplication factor of $\frac{\beta \phi}{\lambda}$ is referred to as the diffusive resistance. In saturated porous media, the diffusive resistance of any non reacting solute ranges from 0.01 to 0.4 (Saripalli *et al.*, 2002). In this work we shall use diffusivity of a free medium as this is a close approximation of that in the LaBarge; which is a relatively clean formation.

Ideal and Real Mixtures

As opposed to a real mixture, an ideal mixture is one which does not show any excess thermodynamic quantities. Molar volumes and molar free energy are examples of some of these quantities. In an ideal mixture there is no volume change when the two or more substances dissolve to form the mixture (Anderson and Crerar, 1993). Thus, the molar volume of the mixture is the weighted average of the molar volumes of its constituents. The change in volume that occurs in real mixing is attributed to the chemical potentials of the mixture. Ideal mixtures are hypothetical models which are only used for simplicity (as this requires less complicated thermodynamic parameters) when they are deemed a good approximation for a real mixture.

In the case of gravity and molecular diffusion, real mixtures differ from ideal ones by the presence of excess molar volumes and the thermodynamic factor (Γ). The thermodynamic factor affects the molecular diffusion part of the separation-mixing equation. It is a function of the gradient of the activity coefficient (γ_A) with respect to mole fractions:

$$\Gamma_{AB} = \delta_{AB} + x_A \frac{\delta \ln \gamma_A}{\delta x_B} \Big|_{T,P} \quad (22)$$

where δ_{AB} is the Dirac delta function, ($\delta_{AB} = 1$ if $A = B$ and $\delta_{AB} = 0$ if $A \neq B$) (Bird *et al.*, 2002). In the case of an ideal mixture, Γ is equal to 1.

To implement the activity coefficient used in the computer program, we used the Porter's equation. This equation is also referred to as the Margules equation and is based on eq. (22) that relates excess Gibbs energy to the activity coefficient (Firoozabadi, 1999):

$$G_E = RT \sum_{i=1}^c x_i \ln \gamma_i \quad (23)$$

The Redlich-Kister expansion for excess Gibbs energy gives (Smith *et al.*, 2001):

$$\frac{G_E}{x_1 x_2 RT} = B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots \quad (24)$$

when $B = C = D = \dots = 0$, $\frac{G_E}{RT} = 0$, $\ln \gamma_1 = 0$ and $\ln \gamma_2 = 0$. In this event $\gamma_1 = \gamma_2 = 1$. An activity coefficient of 1 indicates that the solution is ideal.

If, $C = D = \dots = 0$, then:

$$\frac{G_E}{x_1 x_2 RT} = B \quad (25)$$

where B is constant for a given temperature. The corresponding equations for the activity coefficients are:

$$\begin{aligned} \ln \gamma_1 &= Bx_2^2 \\ \ln \gamma_2 &= Bx_1^2 \end{aligned} \quad (26)$$

Eq. (26) above is referred to as Porter's equation.

The excess molar volumes are the difference between the molar volumes of the a real mixture and an ideal one of the same composition. This affects the non-ideality of gravity part of the separation-mixing equation. Besong (2010) observed that the implementing excess volumes have a negligible effect on the component segregation. Therefore, we shall not take this parameter into account when analysing real mixtures. It is safe to assume that for a given component the partial molar volume is equal to the molar volume ($\bar{v}_A = v_A$). In this work we shall only investigate the impact of the thermodynamic factor when investigating the separation in a real mixture.

Initial Conditions

The numerical and the analytic method (which will be discussed in the next section) were used to solve the separation-mixing equation for three different initial conditions (see Fig.1).

1. Uniform mole fraction with depth,
2. Uniform gradient of mole fraction with depth and
3. Step function of mole fraction.

These three cases can be related to different reservoir filling scenarios.

- Case 1: This indicates a reservoir which is filled by two different fluids at the same time and rate.
- Case 2: A reservoir which was filled with one fluid then later charged with another, a step function like mole fraction profile will be developed.
- Case 3: Gradual charging of a reservoir that already contains a fluid will lead to a reservoir with uniform gradient of mole fraction with depth.

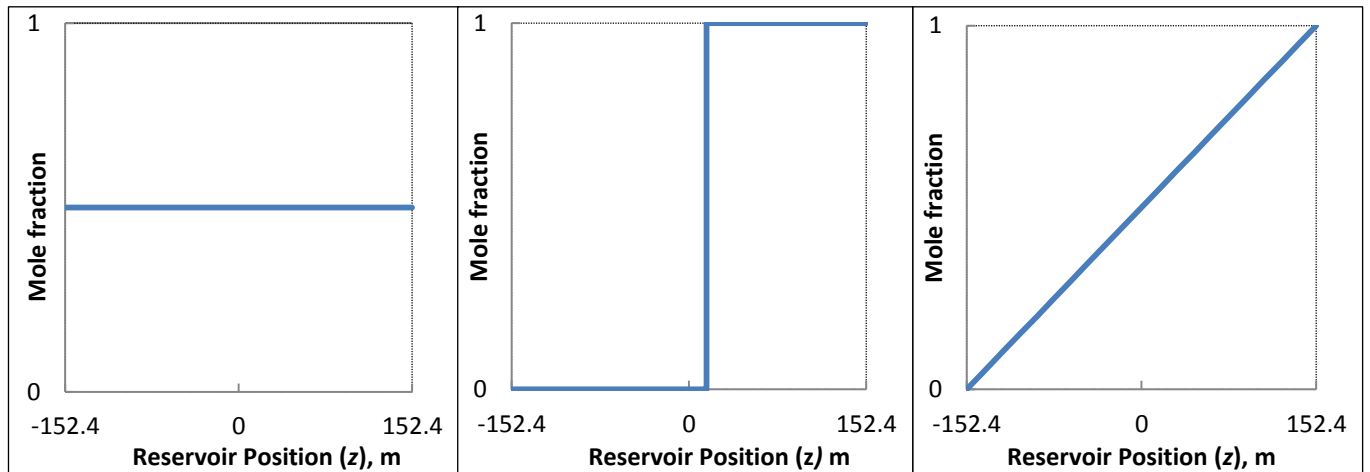


Figure 1: Different reservoir filling scenarios expressed as initial conditions for the numerical and analytical method. The graph relates the initial mole fraction as a function of reservoir depth ($-L \leq z \leq L$). From left to right: uniform mole fraction with depth, step function of the mole fraction and uniform gradient of mole fraction with depth.

Analytical Method

A new analytic steady state solution for an ideal component mixture was derived by Besong (2010). This explicit solution was obtained by applying mass conservation to the ideal separation-mixing equation. The ideal form of eq. (15) is obtained when Γ is equal to 1, and the partial molar volume is equal to the molar volume ($\bar{v}_A = v_A$). The derivation of the analytic solution is summarised in the appendix C.

The solution gives the mole fraction of a given component as a function of the position (height) in the 1-D reservoir:

$$x_i(z) = \frac{\theta_i \overline{2x_i} L}{(e^{2\theta_i L} - 1)} \quad (27)$$

where θ_i is defined as

$$\theta_i = \frac{\rho v_i - M_i}{RT} g \quad (28)$$

and $\overline{x_i}$ is the average distribution of the mole-fractions at the initial state of the reservoir (before the segregation). Besong (2010) derived the analytic solution for only one initial condition (the uniform mole fraction with depth), during the course of this work this solution was modified for the other two initial reservoir conditions.

For a given ideal binary system, the steady state composition is mainly affected by $\overline{x_i}$. For an initial uniform system, this is simply the constant initial mole fraction of a given component in the reservoir, x_i^0 . In the case where the initial distribution of the component in the reservoir varies in a step function manner or has a uniform gradient with depth; $\overline{x_i}$ is strongly governed by the molar volumes of the components. For a system with an initial mole fraction profile identical to the shape of a step function (case 3), $\overline{x_i}$ can be found by:

$$\overline{x_i} \approx \frac{v_j}{v_j + \frac{y_j}{y_i} v_i} \quad (29)$$

where y_j is the initial fraction if the reservoir the component occupies. Refer to appendix C for the derivation of eq. 29 and that for a system with a uniform gradient of mole fraction with depth.

Case Study – LaBarge Field

The LaBarge Field is located in the Sublette County in south-western Wyoming, U.S.A. It is located in the Greater River Basin along the regional north-south trending anticline called Moxa Arch. The field occupies the crestal position along the most northern part of the anticline (see **Fig. 2**). The primary pay interval is the Madison formation, a deep Paleozoic Mississippian carbonate formation, composed of anhydrite and dolomite sequences interbedded with limestone (Huang *et al.*, 2007). The porosity and permeability of the reservoir is primarily governed by the facies. Reservoir quality varies and generally improves towards the crest of the structure.

LaBarge is a gas field with the original gas-water contact (GWC) logged at 9,800 ft TVDSS (2987 m). The gas bearing part of the reservoir ranges from 5,700 ft TVDSS (1737 m) down to the GWC; giving a reservoir height of approximately 1,200 m. In this work $H = 2L = 1200$ m; therefore $-600 \text{ m} \leq z \leq 600$ m. The reservoir has a gross thickness of 800 ft (244 m) with an average net pay of 250 ft (76 m).

The gas compositions at the LaBarge Madison are unusual in that non-hydrocarbon (CO_2 , H_2S , N_2 and He) gases make up nearly 80% of the total, with methane constituting of the remainder near the crest (Huang *et al.*, 2007). Also, the gas compositions vary significantly: methane concentration increases from 5% near the GWC to 20% at the crest. CO_2 decreases from 90% near the GWC to 66% at the crest.

There is little knowledge on how the LaBarge of filled to get this unconventional compositional profile. It has been hypothesised that two different fluids migrated into the LaBarge structural trap almost simultaneously about 50 million years ago (Ma): the first being methane rich containing a significant amount of CO_2 (40 %), and the second was almost entirely CO_2 (10 % of CH_4); and subsequent mixing of these two fluids by molecular diffusion then resulted in the current compositional gradient at the Labarge. **Fig. 3** shows the current methane profile observed at the Madison formation.

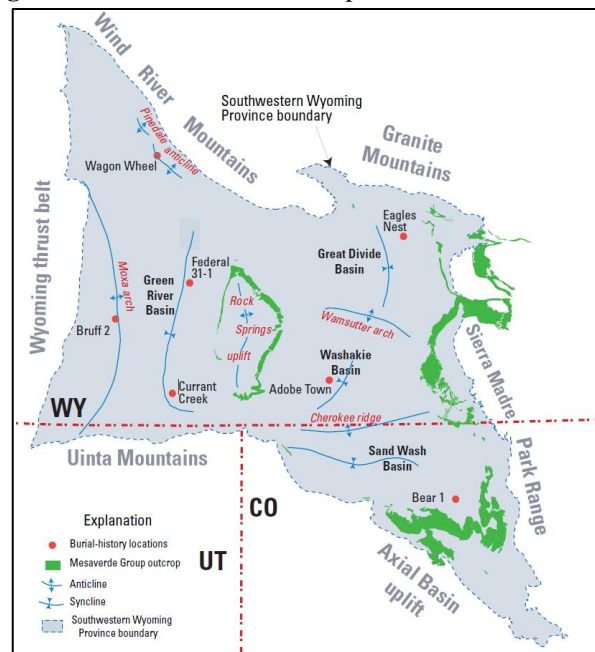


Figure 2: The location of the LaBarge field area with respect to the structural setting of the Greater Green River Basin in the South-western Wyoming Province, Wyoming, Colorado and Utah. (Adapted from Roberts *et al.*, 2005)

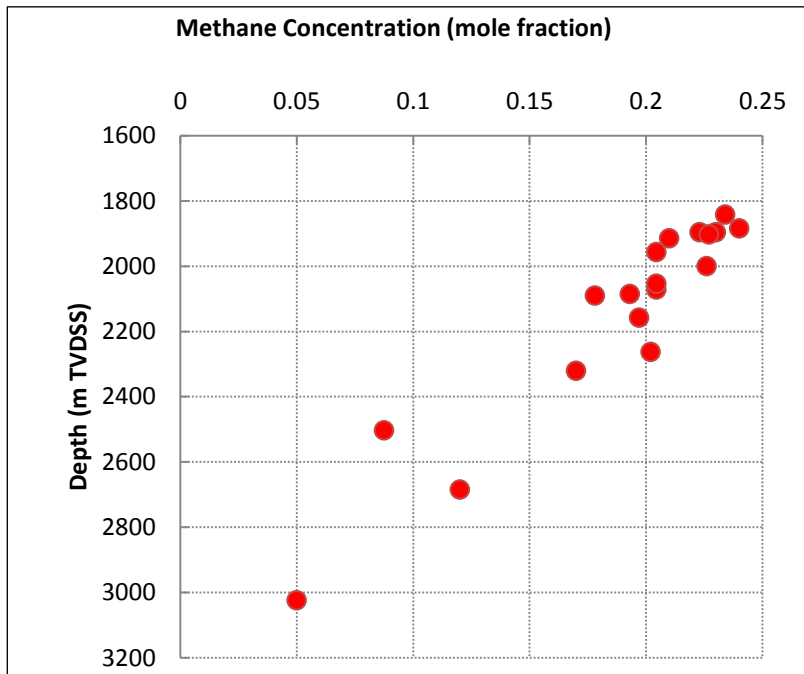


Figure 3: Graph showing the current composition profile observed at the LaBarge Field; CH₄ varies from 5% at the GWC to 23% at the crest. Adapted from IPTC 11202; Huang *et al.* (2007).

Results and Discussion

Methane and carbon dioxide are the two main components present in the LaBarge field, thus we shall be modelling the separation-mixing equation using a binary system of these two components. Due to mass conservation, no material is lost or gained during the segregation process. Therefore, the steady state composition is primarily governed by the average of the initial concentration (\bar{x}_A) of the components in the system. This is in turn affected by the molar volumes of the components. We can therefore find the average initial concentration from the observed LaBarge profile (after segregation), as the average concentration will be the same before and after the separation-mixing process. Applying the trapezium rule to the Labarge profile in Fig. 3, one obtains a \bar{x}_{CH_4} value of 0.14. The initial average concentration used in the numerical and analytical solution and other input parameters are listed in appendix D.

As there is no clear understanding on how the LaBarge got charged with its fluids, we carried out the simulations using two initial conditions; uniform concentration with depth and the step function like mole fraction profile. The composition profiles obtained from the analytical and numerical method for both cases are shown below in Fig. 4. and Fig. 5. Based on eq. 29, it was found that in the case of an ‘initial step function like concentration distribution’ system, CH₄ will have to occupy initially 0.18 of the reservoir (y_j) in order to obtain a \bar{x}_{CH_4} value of 0.14.

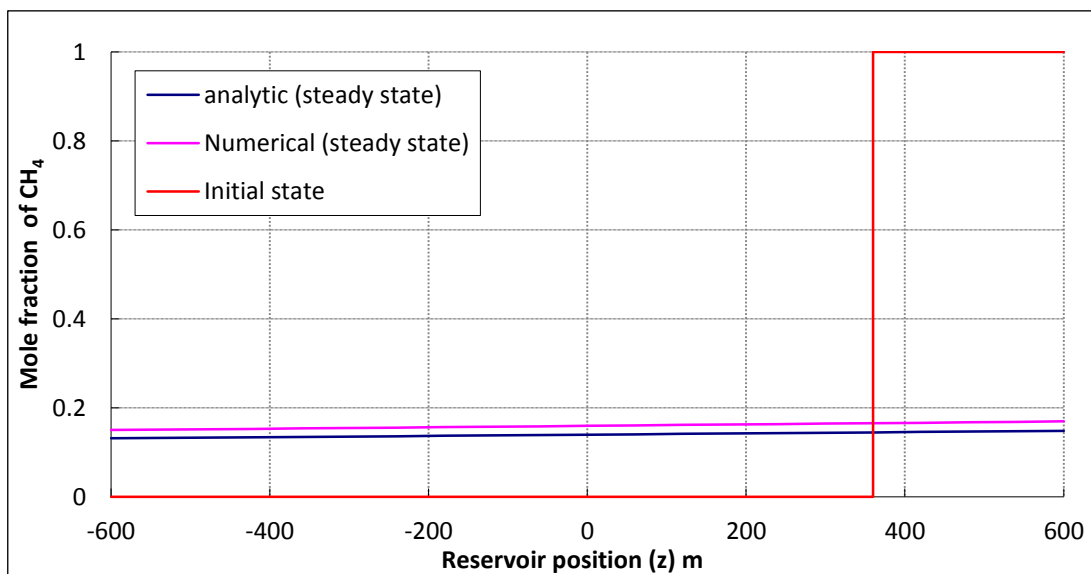


Figure 4: Comparison of the steady state composition profile obtained from the numerical and analytical methods for an ideal mixture of CH₄ and CO₂, with initial concentration profile similar to a ‘step function’. The two methods produce identical profiles.

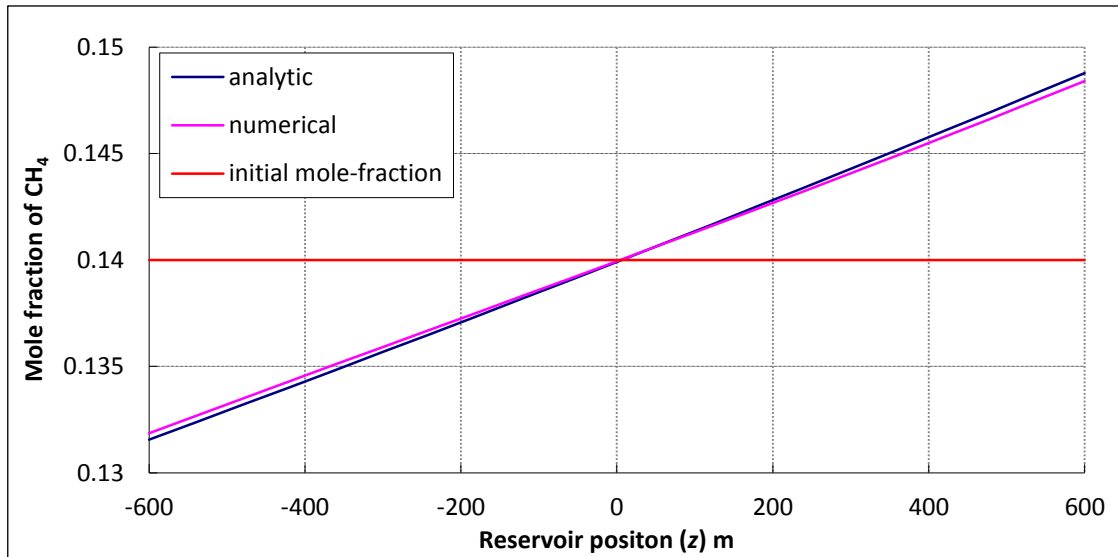


Figure 5: Comparison of the steady state composition profile obtained from the numerical and analytical methods for an ideal mixture of CH₄ and CO₂, with an initial uniform concentration of CH₄ of 0.14. the two methods produce identical profiles.

The two profiles show that in an ideal mixture the composition of CH₄ varies from 0.132 at the bottom to 0.148 at the top of the reservoir. The two cases obtained the same compositional profile as the initial condition does not affect the steady state composition. It can also be seen that the numerical and analytic solutions produce almost identical profile for the ideal mixture segregation. For the ‘step function mole fraction profile’ and uniform mole fraction cases, the numerical solution yields an equilibrium time of 22.7 and 10.6 million years respectively. The segregation obtained in the two cases above (Fig.4 and 5) are too small compared to that observed at the LaBarge (Fig. 3). Therefore the impact of non-ideality on the segregation was investigated.

As stated earlier, the main cause of non-ideality in the case of gravity and molecular diffusion is the thermodynamic factor (Besong, 2010). This can be implemented in the numerical solution as the derivative of the natural logarithm of the activity coefficient with respect to mole fraction. The activity coefficients for a CH₄ and CO₂ mixture at 410 K and 448 bar were calculated using the REFPROP 8.0 program (Lemmon *et al.*, 2007). This was then entered into the computer program (numerical method) by fitting the activity coefficients to Porters equation (eq. 26). The correlation obtained from Porter’s equation is shown in Fig. 6:

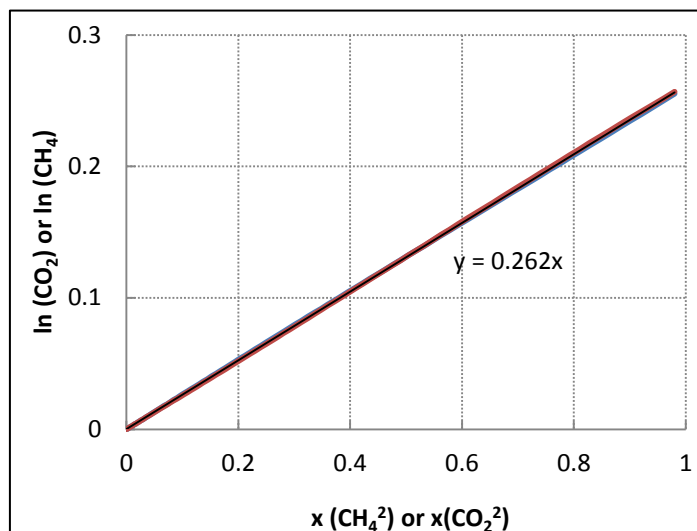


Figure 6: Implementation of the Porters Equation, eq. (26). The Porters constant, B of 0.262 obtained from gradient of the plot.

It can be observed from figure. 6 that the plots for ‘ln CH₄ against x(CO₂)²’ and ‘ln CO₂ against x(CH₄)²’ overlap. The Porters equation constant B (from eq. (26)) was found to be 0.262. The correlation using Porters equation was then used by the computer program to calculate the activity coefficient for any given concentration during the simulation run. The

thermodynamic factor was then calculated and used in the separation-mixing equation. The segregation for a real mixture was thus found (see Fig. 7):

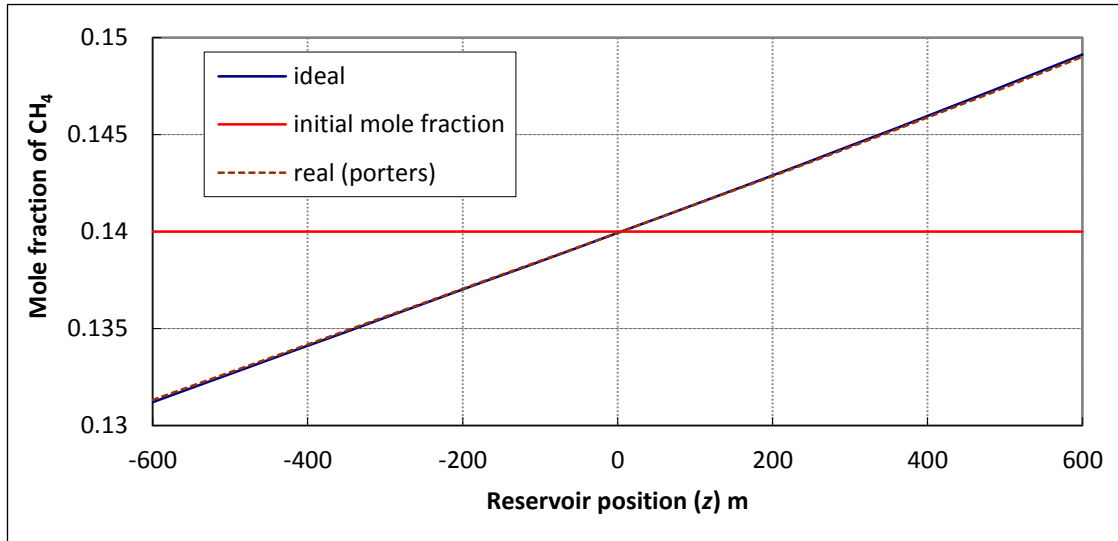


Figure 7: Comparison of the segregation attained in the LaBarge for ideal and real mixtures. The two cases produce identical composition profiles. This shows the mixture of CH₄ and CO₂ at 410 K and 448 bar is close to ideal.

It can be observed from Fig. 7 that the steady state composition profile for the real mixture is identical to that of the ideal case. This was expected as the activity coefficients calculated from REFPROP 8.0 (Lemmon *et al.*, 2007) were approximately 1 for both CO₂ and CH₄ for all the different mixture concentration. This is indicative that the binary mixture is close to being ideal.

The effect of non-ideality was further analysed by increasing the Porter's equation constant B , as this makes the mixture more non-ideal. This was carried out to also investigate the effect of errors in the activity coefficients obtained from REFPROP 8.0. Fig. 8 shows the equilibrium profiles for the binary mixtures for different values of B . It can be observed that the segregation was still very small and similar to the ideal case even when B was doubled. A significant increase in the separation is only noticed when $B = 3$. This however does not reproduce the segregation observed at the LaBarge.

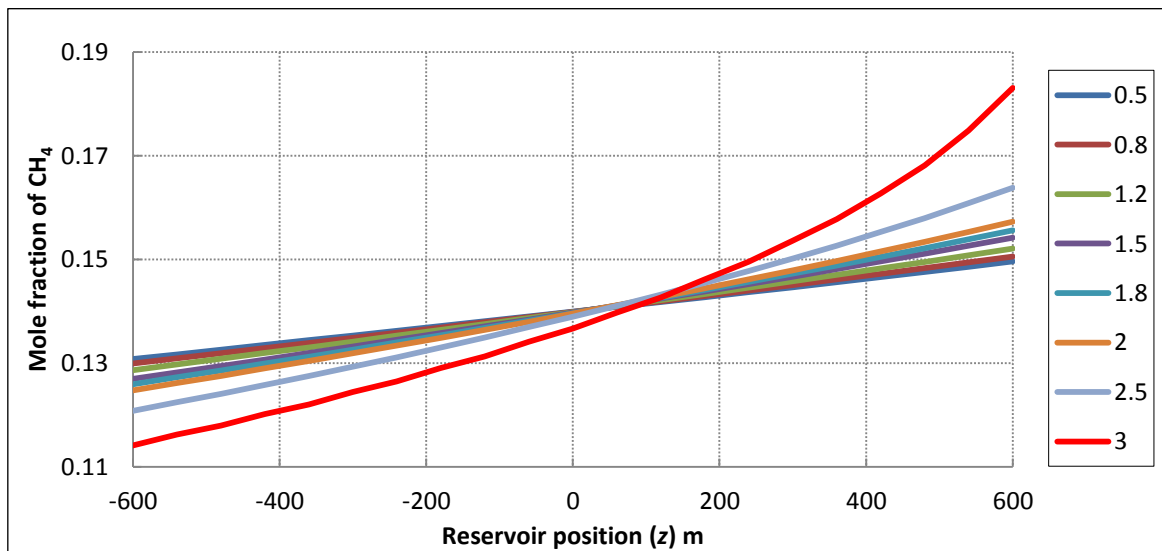


Figure 8: Graph comparing the segregation produced for different Porters equation constant, B . B was varied from 0.5 to 3 to investigate the impact of increasing the non-ideality of the mixture.

Combining Porter's equation and the thermodynamics expression for chemical potential, the Porter's equation constant, B required to obtain segregation currently observed at the LaBarge field can be estimated.

The chemical potential (μ_i) can be defined for a non-ideal solution as (Firoozabadi, 1999):

$$\mu_i(T, P, x) = \mu_i^0(T, P) + RT \ln x_i \gamma_i \quad (30)$$

At equilibrium conditions, the chemical potential can be expressed as:

$$\mu_i = -M_i g z \quad (31)$$

Therefore:

$$\mu_1^{top} - \mu_1^{bottom} = -M_1 g H \quad (32)$$

$$RT \ln \left(\frac{x_1^{top} \gamma_1^{top}}{x_1^{bot} \gamma_1^{bot}} \right) = -M_1 g H \quad (33)$$

Expressing γ in terms of x from eq. (26), the above equation can be rearranged to calculate B .

$$B = \frac{1}{x_{CO_2}^{2(top)} - x_{CO_2}^{2(bot)}} \left[-\frac{M_1 g H}{RT} - \ln \frac{x_{CH_4}^{top}}{x_{CH_4}^{bot}} \right] \quad (34)$$

Normalising the compositions observed in the LaBarge for a binary mixture of CH₄ and CO₂, we obtain a mixture where CH₄ varies from approximately 23% at the top to 5% at the bottom (GWC). Implementing eq. (34) yields a Porters constant B of 5.1. However it was found that values of B greater than 2 may lead to the occurrence of two phase equilibrium (Smith *et al.*, 2001). LaBarge is a gas field; therefore a Porters constant of 5.1 indicating the presence of two-phases is not a valid solution. We therefore conclude that the steady state observed currently at the LaBarge cannot be produced solely by gravity and molecular diffusion. We shall therefore look into other fluxes that may be acting on the fluid in this reservoir and estimate their impact on the segregation.

As discussed earlier, thermal diffusion c a key role in the segregation of the fluids in a reservoir; it either enhances or weakens the separation produced by pressure/gravity diffusion. The impact of thermal diffusion on the composition gradient can be investigated using the total mass flux equation shown in Bird *et. al.*, (1960) and Ghorayeb and Firoozabadi (1999).

$$\bar{J}_1 = (-n^2/\rho)M_1M_2D_{12} \times \left[\left(\frac{\partial \ln f_1}{\partial \ln x_1} \right)_{T,P} \nabla x_1 + \frac{M_1 x_1}{RT} \left(\frac{\bar{V}_1}{M_1} - \frac{1}{\rho} \right) \nabla P + K_T \nabla \ln T \right] \quad (35)$$

where n is the total molar density, ρ is the mass density, D_{12} is the molecular diffusion coefficient for the binary mixture, f is the fugacity and k_T is the thermal diffusion ratio of component 1 and M is the molecular weight. The above equation consists of three parts: molecular diffusion, pressure (gravity) diffusion and thermal diffusion (from left to right). The combined effect of gravity segregation and thermal diffusion in the 1D vertical direction for a binary mixture at steady state is governed by $J_{1z} = 0$. Applying this to eq. (35) and $dP/dz = -\rho g$ (hydrostatic pressure gradient), we obtain:

$$\frac{dx_1}{dz} = \left(\frac{\partial \ln x_1}{\partial \ln f_1} \right)_{T,P} \left[\frac{g x_1}{RT} (\rho \bar{V}_1 - M_1) + K_T \frac{d \ln T}{dz} \right] \quad (36)$$

The thermal diffusion coefficient is the most important parameter when dealing with thermal diffusion as it governs whether the process enhances or weakens the separation in the system. It is defined as:

$$\alpha = \frac{K_T}{x_1 x_2} \quad (37)$$

where α is the thermal diffusion coefficient for component 1. This parameter is nearly independent of composition for low-pressure gases (Firoozabadi, 1999). In low pressure gaseous mixtures and ideal liquid mixtures, α has been found to be small. On the other hand, in non ideal liquid mixtures, this parameter may be large; it becomes very large in the near critical region for both near critical gas and liquid phases. However, at the critical point it has a limiting value (Shulka and Firoozabadi, 1998). It is important to mention that there has been a great deal of confusion in literature in representing the direction of α either in experiment or in theory. For example results from Rutherford and Roof (1959) for a mixture of CH₄ and C₄H₁₀, show that component 1 moves to the hot region when $\alpha > 0$. However in Rutherford work (1963), $\alpha > 0$ means that that component travels to the cold region

There are very few data available in the literature for thermal diffusion coefficient (α) for mixtures of CH₄ and CO₂ at pressures and temperatures as high as that in the LaBarge (448 bar and 410K). We therefore have to use data at close enough conditions to approximate this parameter. Shulka and Firoozabadi (1998) calculated the thermal diffusion constant for an approximately equi-molar mixture of CH₄ and CO₂ at 373 K, with pressures ranging from 10 to 80 bar. The α values were calculated based on a correlation derived by Shieh (1969). At the maximum pressure of 80 bar, α was calculated to be 0.25.

Pal *et al.* (1973) obtained a α value of 0.1 for a binary mixture of CH₄ and CO₂ at 420 K. The methane concentration ($x_{CH_4} = 0.15$) of the mixture used for the analysis is close to that in the LaBarge.

Using the thermal diffusion coefficient of 0.1 and assuming a normal geothermal gradient in the LaBarge (0.3 K/m) as basis of an order of magnitude test using eq. (36), we find that thermal diffusion will produce an equal impact as gravity on the compositional grading of this mixture (see appendix E). As the value of α increases the impact of thermal diffusion will surpass that of gravity segregation. The equation used by Pal *et al.* (1973) to obtain values of α suggests that a positive value of thermal diffusion coefficient (α), would lead to CH₄ travelling towards the ‘hot’ region; in this case to the bottom of the reservoir. This will therefore weaken the separation developed by gravity. However, the thermal diffusion coefficient by Pal *et al.* (1973) was obtained at pressures lower than that in the LaBarge. The mixture of CH₄ and CO₂ in the LaBarge are at super-critical conditions, If this mixture produces negative values of α , then thermal diffusion will enhance the separation.

Another important phenomenon that might affect the composition gradient is natural convection. Natural convection is either concentration or temperature driven, and its effect can be estimated by comparing the characteristic time of this process (t_c) to that of molecular diffusion (t_M). Recall that if the time taken for these two systems to attain equilibrium is similar, the segregation could be significantly enhanced. Applying eq. (5), with α_p of $3.7 \times 10^{-3} \text{ K}^{-1}$, μ of $53.2 \times 10^{-6} \text{ kg/ms}$ (calculated by REFPROP 8.0), k of 100 mD (Hongjun, 2009), ρ of 592 kg/m^3 , $\sin(\beta) = 0.9$ and a normal geothermal gradient; one obtains a characteristic time for natural convection of about 48 million years. This is about double the timescale of molecular diffusion, thus meaning that the effect of convection will not be seen as the process is relatively slow compared to diffusion. The timescale for convection is however close to the currently ‘hypothesised’ age of reservoir filling (50 Ma).

Another major factor that could affect the steady state composition is the structure and properties of the LaBarge field. Barriers or baffles to flow like shales and faults present in the reservoir could delay or impede the attainment of steady-state composition. However, the data obtained for the Madison reservoir shows this not the case; as porosity measurements obtained from Cores and Logs show a good reservoir rock (ϕ ranging from 4 to 26 %). This is also backed up by Gamma-ray (GR) wireline logs (Huang *et al.*, 2007) which shows that the reservoir does not contain any shale layers, as all the 14 logs taken from the Madison reservoir show a consistent low GR reading (see appendix F).

The Madison reservoir is an anticline with a length to thickness ratio of about 5:1. This shape might influence the impact of diffusion and convection process depending on the angle of inclination. If the reservoir was upright (inclined at 90°) the impact of diffusion or convection will be maximum; and the diffusion process will take the amount of time calculated using the numerical solution. As the angle of inclination decreases the effect of these processes will be reduced as the motion paths of the molecules will be obstructed and it will take more time for the fluid to separate to produce the steady state profile.

The filling time of the LaBarge field is another factor that could have a massive impact on the currently observed composition profile. It is hypothesised that the field was charged about 50 Ma. Recall that the numerical solution for a ‘step function like initial concentration profile’ took about 22.7 million years to reach steady state. If the field was charged about 4 to 6 Ma, steady state will not yet be attained. **Fig. 9** shows how the segregation in the LaBarge is developed over time. From closer analysis in **Fig. 10**, it can be seen that at about 4 to 6 million years the numerical solution produces profile similar to that currently observed at the LaBarge field. It can thus be suggested that the reservoir was recently filled about 4 Ma and is still undergoing mixing by molecular diffusion.

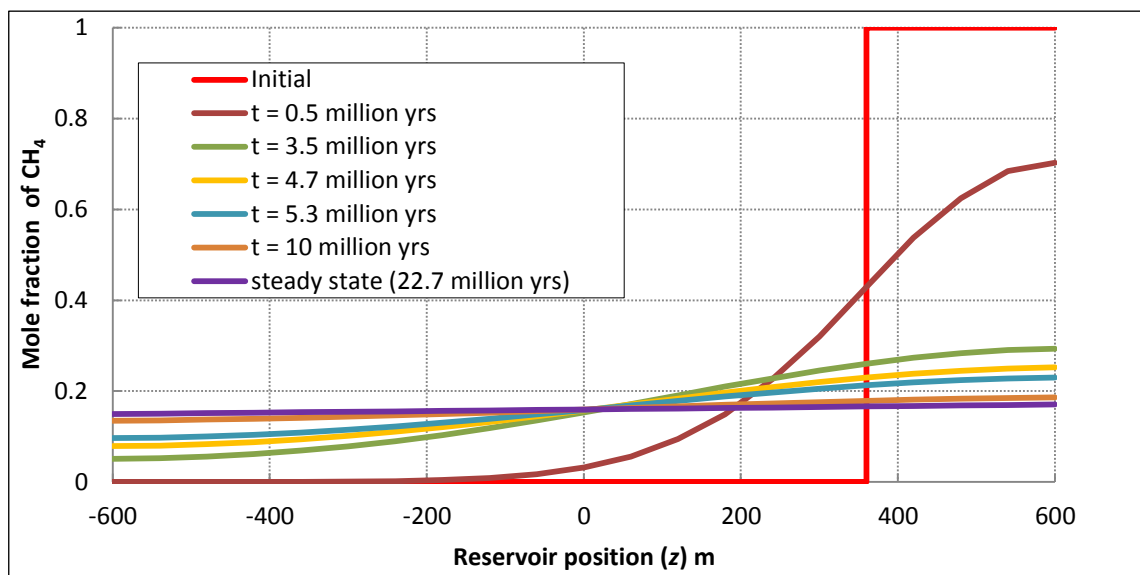


Figure 9: Graph showing the development of steady state over time for a case where the initial concentration varies like a step function.

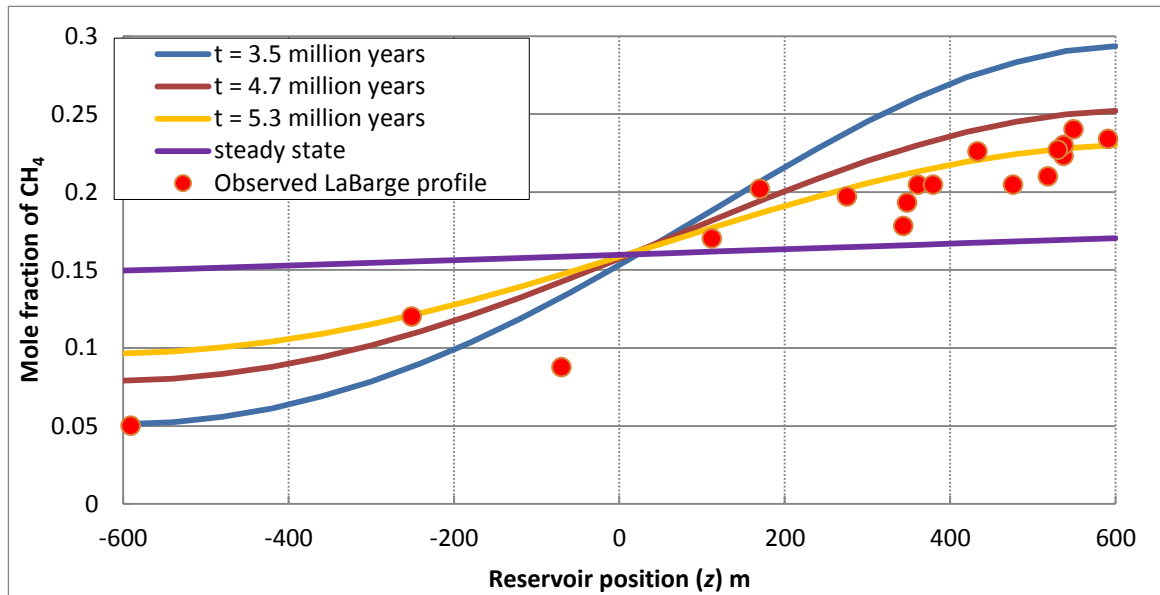


Figure 10: Comparison of composition profile obtained from numerical solution at certain time steps to that observed at the LaBarge field. It is observed that at $t = 5.3$ million years produces a reasonable match to the observed field composition.

Current reservoir filling is another factor that strongly affects the steady state composition profile. If the LaBarge is currently getting filled with fluid; steady state will not be attained as any attempt for molecular diffusion or convection to homogenise the composition profile will be hampered by the addition of more fluid into the reservoir. It will thus be impossible to predict the profile if this was the case based on the irreversible thermodynamics used in this work, as they are derived at steady state.

In this work, a binary mixture of CH_4 and CO_2 was investigated (as these were the main components) alone not accounting for the impact the other components will have on the mixture in the LaBarge. H_2S is the next major component in the LaBarge field. If this study was carried out using the ternary system of H_2S , CH_4 and CO_2 ; the addition of H_2S will increase the non-ideality of the current mixture and might lead to an increase in gravitational segregation. However, it has been previously explained that increasing the non-ideality of the mixture will not produce the supposed steady state compositional profile observed at the LaBarge field.

Conclusion

This work has investigated the effect of gravity and molecular diffusion on the compositional gradients in the LaBarge field using separation-mixing equation derived from irreversible thermodynamics. This equation was implemented into numerical and analytic solutions, which were used to produce steady-state composition profiles to compare with the composition profile observed currently at the LaBarge. The numerical solution was used to find the time to attain this steady state as the time at which the LaBarge got filled is currently not fully known.

The profiles obtained from the two solutions for a binary mixture of CH_4 and CO_2 at the LaBarge conditions, were different from that observed currently at the field. We can therefore conclude:

- Gravity and molecular diffusion alone cannot achieve the separation currently observed at the LaBarge (assuming the LaBarge has actually achieved steady state).
- Other fluxes like natural convection and thermal diffusion might have affected the fluid in the LaBarge to produce the composition profile currently observed.
- From the results obtained, the most logic conclusion is that the LaBarge was filled recently; about 4 million years ago as opposed to 50 million years ago as originally thought. Thus, steady state which should be achieved in approximately 22.7 million years has not been achieved and the reservoir is still undergoing the effect of gravity and molecular diffusion.

Further work is needed to investigate more thoroughly the impact the structure of the reservoir might have on the separation-mixing process. I suggest that 2-D simulations with more rigorous reservoir modelling should be carried out to investigate the impact the reservoir structure may have on the diffusion processes. I also suggest the impact of natural convection and thermal diffusion (with accurate values of thermal diffusion constants) have on the LaBarge field be investigated.

Nomenclature

| | |
|---------------|--|
| c_A | Molar concentration of component A, mol/m ³ |
| c | Molar concentration of the mixture, mol/m ³ |
| D_{AB} | Molecular diffusion coefficient of component A in B, m ² /s |
| D_f | Molecular diffusion coefficient in free space, m ² /s |
| f | Fugacity, N/m ² |
| g | Acceleration due to gravity, m/s ² |
| G_E | Gibbs free energy, J |
| h | Reservoir thickness, m |
| J | Molar flux, mol/m ² s |
| k | Permeability, mD |
| k_T | Thermal diffusion ratio |
| L | Half the thickness of the reservoir, m |
| M_A | Molecular weight of component A, g/mol |
| R | Universal gas constant, 8.413 J/mol.K |
| t | Time, s |
| T | Temperature, K |
| v_A | Molar volume, m ³ /mol |
| \bar{v}_A | Partial molar volume, m ³ /mol |
| β | Constriction factor |
| \bar{x}_A | Average distribution of mole fraction at initial conditions |
| x_A | Mole fraction |
| y_A | Volume fraction occupied by component A |
| z | Vertical coordinates along the reservoir, m |
| P | Pressure, N/m ² |
| α | Thermal diffusion coefficient |
| α_p | Thermal expansion coefficient, 1/K |
| δt | Time scale, sec |
| δz | Grid size, m |
| μ | Viscosity, Pa.s |
| μ_i | Chemical potential of component A, J/mol |
| δ_{AB} | Dirac delta function |
| ϕ | Porosity |
| γ_A | Activity coefficient of component A |
| Γ | Thermodynamic factor |
| λ | Tortuosity |

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Appendix

APPENDIX A: Literature Reviews

Journal of Petroleum Science and Engineering 58, 391-402

Initial state of petroleum reservoirs: A comprehensive approach.

Authors: Montel F., Bickert J., Lagisquet A. and Galliero G.

Contribution to the understanding of fluid distribution in the reservoir:

This paper explains in depth the main fluxes that affect the fluid in the reservoir, highlighting the ones that tend to lead to fluid separation (thermal diffusion and pressure diffusion); and those that tend to homogenise the fluid content in the reservoir (molecular diffusion and convection).

It shows how to tell which flux is more dominant (molecular diffusion or natural convection) by comparing time-scales:

$$t_M^A = \frac{H^2}{D_A}$$

$$t_C = \frac{\mu}{\rho g k \alpha_p \nabla_z T \sin(\beta)}$$

- $t_C \gg t_M^A$: No or very slow convection occurs.
- $t_C \ll t_M^A$: Very active convection; the homogenous fluid profile in the whole reservoir.
- $t_C \leq t_M^A$: Segregation process should be significantly increased when there is a similar timescale for natural convection and diffusion in the reservoir.

Objective of the paper:

To present the equations for modelling stationary state of a reservoir under the impact of all possible fluxes; diffusion (thermal, pressure and thermal) and natural convection.

Methodology used:

This paper used irreversible thermodynamics to obtain the equations to model the fluxes at on a steady state reservoir.

Conclusion:

- Integrating reservoir constraints during evaluation of the fluid distribution is compulsory and the estimated external fluxes have to be confirmed by other well data, like mud gases.
- In the case where there is pressure or temperature change in the reservoir, the flux model can still be used, but the local fluxes required for modelling have to be consistent with the overall process at geological time scale.
- Discrepancies to modelling will arise when permeability barriers are present in the reservoir.

Ind. Eng. Chem. Res. 1998, 37, 331-3342

A new model of thermal diffusion coefficients in binary hydrocarbon mixtures

Authors: Shulka, K. And Firoozabadi, A.

Contribution to the understanding of the thermal expansion process:

This paper provides results of thermal diffusion for the modelling of various mixtures as a function of temperature and concentration. Most importantly it provides results for methane and carbon dioxide mixtures. These show that as the pressure increases the thermal diffusion coefficient becomes more positive.

Objective:

To present a simple analytic model of thermal diffusion coefficients in binary mixtures and examine its accuracy by comparing theoretical results with available experimental data.

Methodology used:

The method used for the correlation of the thermal diffusion coefficient was based on the thermodynamics of irreversible processes.

Conclusion reached:

- This model was more rigorous than those presented in the past.
- Detailed comparisons of theoretical results with experimental data for the thermal diffusion coefficients show the good performance of the model in different non-ideal conditions but away from the critical region.

Comments:

This model fails along with others at predicting thermal diffusion coefficient at the near critical region.

IPTC 11202

Integrated reservoir modelling to maximise the value of a large sour-gas field with high concentration of inerts

Authors: Huang, N.S., Aho, G/.E. and Baker, B.H.

Contribution to my knowledge to the LaBarge Field:

This paper analysis the properties and structure of the LaBarge filed. Most importantly it explains the hypothesis to the unusual component distribution.

It specifies the gas composition of the LaBarge field; 20% of methane at the crest to near 5% at the GWC; and 66% of carbon dioxide at the crest to 90% at the GWC. It also provided the profile of the current fluid distribution in the field; which was used as a basis of our simulation.

Objective of the paper:

To discuss the integration of reservoir characterisation studies, geochemical analysis, surveillance data, reservoir simulation and surface facility network models to optimise the near time development plan and evaluate potential expansion.

Conclusion:

- The initial vertical compositional gradient may be caused by the trap charging with fluids from two different sources: the first fluid being methane-rich, the second fluid being carbon dioxide rich; followed by gradual diffusion for 50 million years.

Comments:

This paper was only useful in getting information about the field as it focuses on gas production while dealing with H₂S and CO₂.

SPE 63085

Compositional Grading- Theory and Practice

Authors: Høier, L., and Whitson, C.H.

Contribution to the understanding of compositional grading:

This paper summarises all the possible causes of fluxes that can lead to compositional distribution in a reservoir. It highlights other factors other than diffusion and convection; migration, leakages, biodegradation, asphaltene precipitation and multiple source rocks to name a few.

Objective of the Paper:

This paper quantifies the potential variation in composition and PVT properties with depth due to gravity, chemical and thermal forces.

Methodology used:

This paper also used the thermodynamics of irreversible processes for a steady state to investigate the cause of fluid distribution in a convective- free system.

Conclusion:

- Thermal diffusion generally counteracts gravity, resulting in compositional gradients with depth which smaller than the predicted with the isothermal model.
- For near critical, near saturated systems, thermal diffusion may be large compared with gravitational segregating forces.

SPE 11761, 1983

The effect of gravity and temperature gradients on methane distribution in oil reservoirs

Authors: Holt, T., Linderberg, E., and Ratkje, S.K.

Contribution to knowledge of fluid segregation in the reservoir:

With the use of irreversible thermodynamics, it was found that the thermal diffusion is usually of the same magnitude as gravitational segregation. In critical oil reservoirs, closer to critical conditions, temperature effect (thermal diffusion) dominates.

Objective of the paper:

To study the effect of gravity and thermal diffusion in a convection-free system.

Methodology used:

This work utilises irreversible thermodynamics for a stationary system.

Conclusion:

- Thermal diffusion has similar impact on the fluid segregation as gravity separation.

Journal of the Geological Society 1987, 144, 327 – 347

The movement and entrapment of petroleum fluids in the subsurface

Authors: England, W.A., Mackenzie S.A., Mann, D.M., Quigley, T.M.

Contribution to knowledge of reservoir filling:

It explains the whole process of reservoir charging from the formation of kerogen, the migration of mobile crude oil and to the accumulation in the trap. It explains the concept of ‘petroleum potential’; the driving force for migration.

It also briefly explains how molecular, gravity, and thermal diffusion affect the fluid after accumulation in the reservoir.

Objective:

To discuss the migration of petroleum fluid from its source rock to its possible entrapment in a reservoir.

Comments:

- In a liquid petroleum accumulation, convection is not a significant process.
- As petroleum migrate, vertical movement will lead to changes in temperature and pressure; which will lead to subsequent changes to volumes of oil and gas.

SPE 9235

Compositional variations within a hydrocarbon column due to gravity

Author: Schulte, A.M.

Contribution to understanding the modelling of gravity effects on the reservoir:

This paper only takes gravity into account. It provides equations used to model a steady state system which under the influence of gravity based on the gravity potential.

$$d\mu_i + m_i g dh = 0$$

It shows how equilibrium can be determined by the difference in chemical potentials:

$$\mu_i(h = h_2) - \mu_i(h = h_1) + m_i g (h_2 - h_1) = 0$$

Objective:

To achieve a more satisfactory solution for composition variation for non ideal fluids.

Methodology used:

This used the Soave equation, with and without binary interactive parameters and Peng-Robinson equation of state to find the chemical potentials.

Conclusions:

- It is possible to calculate the compositional gradient in hydrocarbon columns accurately using this method.
- Composition variation in an oil column depends on pressure.
- The predicted effect of gravity on composition is sensitive to interactive coefficients used in the equation of state.

Imperial College PhD Thesis, 2010

Time-scales for the development of thermodynamic equilibrium in hydrocarbon reservoirs

Author: Besong, D.

Contribution to the understanding of the Numerical and analytic solution for the separation-mixing equation:

This thesis provides a completely overview into the separation mixing process by gravity and molecular diffusion.

It provided the formulation of the equation that govern the separation for both ideal and real mixtures.

Objectives:

- To develop analytical and numerical tools for molecular and gravity diffusion in a single phase system which are close representative of a real system as possible.
- Carry out sensitivities of the time-scales and composition to various parameters.

Method:

This paper used irreversible thermodynamics to model the impact of gravity and thermal diffusion.

Conclusion:

- Excess molar volume which affects the non-ideality of the gravity term in the segregating equation has negligible effect on separation.
- Increasing reservoir height, increases the separation.

Comments:

This paper provides an explicit solution to the gravity and molecular diffusion system; most previous methods are implicit, which require iterations.

AIME (1939), 132, 120 - 131

Gravitational concentration gradient in static columns of hydrocarbon fluids

Authors: Sage, B.H and Lacey, W.N.

Contribution to understanding of gravity segregation:

This paper pioneered the investigation of the impact of gravity on fluid distribution. This present the original thermodynamic equations which have been modified by

Objective of the paper:

To investigate the impact of gravity on a binary hydrocarbon liquid and a binary hydrocarbon gas

Methodology used:

This uses thermodynamics of irreversible processes for a system at equilibrium.

Comments:

The method was derived for an ideal liquid, therefore there was a lot of simplifications made in this model. However, this simplifications made this method too restrictive.

APPENDIX B: Critical Literature Review

TABLE B1: Table of Milestones for modeling gravity and molecular diffusion

| Journal (year) | Paper No. | Title | Authors | Contribution |
|----------------|-----------|--|---------------------------|--|
| AIME (1939) | 132 | Gravitational concentration gradient in static columns of hydrocarbon fluids | Sage, B.H and Lacey, W.N. | First to analyse the influence of gravity on spatial distribution of components in a reservoir fluid system. (Assuming ideal solutions). |
| SPE (1980) | 9235 | Compositional variations within a hydrocarbon column due to gravity | Schulte, A.M | First to develop a more defined model for gravity segregation, as that by Sage, B.H and Lacey, W.N. was too restrictive due to simplifications made. |
| 2010 | - | Time-scales for the development of thermodynamic equilibrium in hydrocarbon reservoirs | Besong, D. | First to create explicit model to solve for steady state composition and time in a system under the influence of gravity and molecular diffusion. |

APPENDIX C: DERIVATION OF ANALYTIC SOLUTION

Besong (2010) derives an explicit steady state solution to the ideal separation-mixing equation based on mass conservation. For a reservoir of height 2L, where $-L \leq z \leq L$, the total number of moles of each component in the whole reservoir stays constant regardless of the composition profile at any time.

$$\int_{-L}^L cx_i(z) dz = \int_{-L}^L cx_i(-L) e^{\frac{\int_{-L}^z \rho v_i dz - M_i(z+L)}{RT} g} dz = \int_{-L}^L cx_i^0 dz \dots\dots\dots(1)$$

As density does not vary much along the reservoir, molar mass M_i is constant and at steady state the concentration along the reservoir does not vary that much. Therefore the above equation can be simplified taking c and $\frac{RT}{(\rho v_i - M_i)g}$ as approximately constant.

$$\int_{-L}^L x_i^0 dz = \int_{-L}^L x_i(-L) e^{\frac{\int_{-L}^z \rho v_i dz - M_i(z+L)}{RT} g} dz \dots\dots\dots(2)$$

$$\approx \frac{x_i(-L)}{\theta_i} (e^{2\theta_i L} - 1)$$

Where

$$\theta_i = \frac{\rho_{(average)} v_i - M_i}{RT} g \dots\dots\dots(3)$$

Rearranging this equation yields,

$$x_i(-L) \approx \frac{\theta_i \int_{-L}^L x_i^0 dz}{(e^{2\theta_i L} - 1)} \dots\dots\dots(4)$$

Thus we obtain a general expression for the steady-state mole-fraction of each component at every point in the reservoir.

$$x_i(z) \approx \frac{\theta_i \int_{-L}^L x_i^0 dz}{(e^{2\theta_i L} - 1)} e^{(z+L)\theta_i} \dots\dots\dots(5)$$

Bessong derives this equation only for system with uniform initially condition. We shall now modify this equation to deal with the other two initial conditions.

1) UNIFORM INITIAL CONCENTRATION

This is the simplest case as initial mole fraction x_i^0 is constant through out the reservoir. Therefore, we obtain

$$x_i(z) \approx \frac{\theta_i 2x_i^0 L}{(e^{2\theta_i L} - 1)} e^{(z+L)\theta_i} \dots\dots\dots(6)$$

2) STEP FUNCTION LIKE INITIAL CONCENTRATION DISTRIBUTION

In this case, the initial condition is not uniform, thus \bar{x}_i^0 will be taken as the average distribution of the initial condition in space x_i .

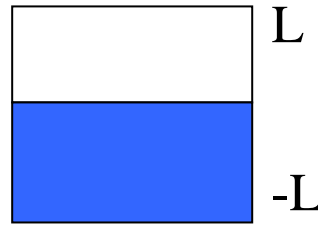


Figure C.1: Illustration of a Reservoir with a step function like initial concentration distribution

Thus,

$$\bar{x}_A = \frac{\int_z^L c x_A(z) dz}{\int_z^L c x_A(z) dz + \int_{-L}^z c x_B dz} \dots\dots\dots(7)$$

This can be simplified by taking the summation of the volume each component occupies in the reservoir.

$$\bar{x}_A \approx \frac{\sum_z^L c_A x_A V_1}{\sum_z^L c_A x_A V_1 + \sum_{-L}^z c_B x_B V_2} \dots\dots\dots(8)$$

The volume term can be expressed as volume fraction of the reservoir each component occupies.

$$\bar{x}_A \approx \frac{y_1 c_A \sum_z^L x_A}{y_1 c_A \sum_z^L x_A + y_2 c_B \sum_{-L}^z x_B} \dots\dots\dots(9)$$

The initial mole fraction of each component in their respective ‘section’ of the reservoir will always be 1. We thus obtain;

$$\bar{x}_A \approx \frac{c_A}{c_A + \frac{y_2}{y_1} c_B} \approx \frac{v_B}{v_B + \frac{y_2}{y_1} v_A} \dots\dots\dots(10)$$

3) INITIAL DISTRIBUTION WITH UNIFORM GRADIENT

In this case, the average distribution of the initial distribution of the initial condition in space is also used in the general equation for the compositional variation.

$$\bar{x}_A = \frac{\int_{-L}^L cx_A(z)dz}{\int_{-L}^L cx_A(z)dz + \int_{-L}^L cx_B dz} \dots\dots\dots(11)$$

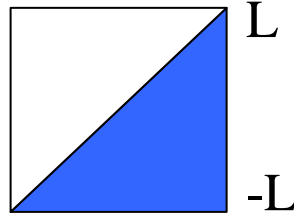


Figure C.2: Illustration of a Reservoir with an initial uniform concentration gradient with depth.

When the mole fraction of component A varies from 0 at the bottom to 1 at the top of the reservoir with a uniform gradient mole distribution, the mole-fraction of component A can be expressed as;

$$x_A = \frac{z + L}{2L} \dots\dots\dots(12)$$

And

$$c = \frac{1}{v} = \frac{1}{x_A v_A + (1 - x_A) v_B} \dots\dots\dots(13)$$

Therefore $\bar{x}_A = \frac{\int_{-L}^L \frac{z + L}{z(v_A - v_B) + L(v_A + v_B)} dz}{\left(\int_{-L}^L \frac{z + L}{z(v_A - v_B) + L(v_A + v_B)} dz + \int_{-L}^L \frac{L - z}{z(v_A - v_B) + L(v_A + v_B)} dz \right)}$ (14)

Integrating this expression yields;

$$\bar{x}_A = \frac{A + B}{2B} \dots\dots\dots(15)$$

Where

$$A = \left[\frac{L}{(v_A - v_B)} \ln \{ (v_A - v_B)z + L(v_A + v_B) \} \right]_{-L}^L \text{ And}$$

$$B = \left[\frac{z}{(v_A - v_B)} - \frac{L(v_A + v_B)}{(v_A - v_B)^2} \ln \{ (v_A - v_B)z + L(v_A + v_B) \} \right]_{-L}^L$$

APPENDIX D: DATA USED TO IMPLEMENT NUMERICAL AND ANALYTIC METHODS

User Guide on Gravity Segregation Software 1 (shown Based on Uniform Initial Concentration, parameters used in Bold)

* * * * *

* Isothermal Isobaric Only

* Molecular and Gravity Diffusion only.

A. The content of input files:

This describes the content of the input files.

Line 1: reservoir thickness in meters: **1200m**

Line 2: number of components: **2, (CO₂ and CH₄, in this order)**

Line 3: number of grid points: **21**

Line 4: initial compositions uniform: (0 = uniform, 1 = varies vertically) **0**

Line 5: the composition of various components

: If 1 is chosen in line 4, then the value in this line represents the component (counting from 1) from which concentration at the bottom of the reservoir is zero. Components before this inclusive has zero concentration at the top.

: If 0 is chosen in line 4,

- Then 0 in this line means equal concentrations for all components

- If 1, the programme asks the user to choose the mole-fraction of the first component, and the rest of the components will have equal mole-fractions.

- If 2, the computer asks for the mole-fraction of component 1, then asks for component 2. The rest of the components will have equal mole-fraction

: **Choose 1; and input 0.86 for initial mole concentration of CO₂; ($\overline{x_{CH_4}}$ of 0.14)**

Line 6: If 1 is chosen in line 4 (ie non-uniform concentrations), 0 here means step functions (at the middle of the reservoir), 1 means uniform gradients. If $0 < \text{value} < 1$, this gives the fraction of the reservoir occupied by component 1. **0**

Line 7: Temperature: **410k**

Line 8: Enter any number. This value is no more valid but deleting it will mean I have to do a lot of work with the code, so just enter any number: **8×10^{-3}**

Line 9: Stopping criterion.: **2.5×10^{-5}**

Line 10: Enter a very large number. It is the maximum number of iterations: **1×10^7**

Line 11: Interval of time-steps to save the solution to files: **10**

Line 12: Which transport processes? if 0, molecular alone; if 1, both molecular and gravity; if 2, gravity alone: In our case we choose **1**

Line 13: Molar volumes (m^3/mol): **6.45×10^{-5}** and **8.67×10^{-5}** for CO_2 and CH_4 respectively.

Line 14: Molar Masses (kg/mol) : **4.42×10^{-2}** and **16.04×10^{-3}**

Line 15: Molar volumes at normal boiling point (cm^3/mol):**15602** and **8809**

Line 16: Viscosities (milli Pascal. second); **0.0579** and **0.0248**

Line 17: Densities (kg/m^3): **683.168** and **184.496**

Line 18: Diffusion resistivity (is a function of tortuosity, porosity and constrictivity) =**1.0** in most of my simulations.

Line 19: Enter 3 values. Which terms or parameters are considered as real. 1=real, 0= ideal.

the first value is for the assumption of equal molar volumes, second value is for molecular diffusion, third value is for gravity diffusion. Note that if you enter 0 for the first value, then you must enter equal molar volumes in line 13 for all components.

(1 0 0) → Simulations for ideal mixture

(1 1 0) → Simulations for Real mixture

Line 20: Activity coefficients to be used. This value is read only if the middle entry of line 19 is chosen to be 1. so the activity coefficients will be calculated from using the Margules equation.

For binary mixtures:

$$1 = c1_c5$$

$$2 = c1_nc11$$

$$3 = c1_mnp$$

$$4 = c5_c11;$$

$$5 = c5_mnp$$

$$6 = \text{CO}_2 \text{ and } \text{CH}_4 \text{ (based on Porters Equation)}$$

Line 21: polynomial constants for the Redlich-Kister polynomial to get excess volumes. This term was not used as we ignored the impact of excess molar volumes.

APPENDIX E: ORDER OF MAGNITUDE TEST TO INVESTIGATE THE IMPACT OF GRAVITY AND THERMAL DIFFUSION

The expression for the total mass flux in a binary system for component 1 is given by Bird et al.(1960), and Ghorayeb and Firoozabadi (1999):

$$\vec{J}_1 = (-\eta^2/\rho)M_1M_2D_{12} \times \left[\left(\frac{\partial \ln f_1}{\partial \ln x_1} \right)_{T,P} \nabla x_1 + \frac{M_1 x_1}{RT} \left(\frac{\bar{V}_1}{M_1} - \frac{1}{\rho} \right) \nabla P + K_T \nabla \ln T \right]$$

Where η is the total molar density, ρ is the mass density, D_{12} is the molecular diffusion coefficient for the binary mixture, f is the fugacity and k_T is the thermal diffusion ratio of component 1 and M is the molecular weight. The above equation consists of three parts: molecular diffusion, pressure (gravity) diffusion and thermal diffusion respectively.

The combined effect of gravity segregation and thermal diffusion in the 1D vertical direction for a binary mixture at steady state is governed by $J_{1z} = 0$. Applying this to Eq. and $dP/dZ = -\rho g$, we obtain:

$$\frac{dx_1}{dz} = \left(\frac{\partial \ln x_1}{\partial \ln f_1} \right)_{T,P} \left[\frac{gx_1}{RT} (\rho \bar{V}_1 - M_1) + K_T \frac{d \ln T}{dz} \right]$$

The above equation will be utilised to find out what diffusion process has a bigger impact on the composition gradient for binary mixture of CH_4 and CO_2 . First the thermal diffusion ratio has to be defined. This is a measure of thermal diffusion and the sign of k_T determines the direction of thermal diffusion. Thermal diffusion ratio can be found by:

$$K_T = \alpha x_1 x_2$$

Where α is the thermal diffusion factor.

Expressing $\left(\frac{\partial \ln x_1}{\partial \ln f_1} \right)_{T,P}$ as a constant A and applying the chain rule to $\frac{d \ln T}{dz}$, one obtains:

$$\frac{dx_1}{dz} = A \left[\frac{gx_1}{RT} (\rho \bar{V}_1 - M_1) + K_T \frac{1}{T} \frac{dT}{dz} \right]$$

The gravity term is given by;

$$\frac{gx_1}{RT} (\rho \bar{V}_1 - M_1)$$

While the thermal diffusion term is;

$$K_T \frac{1}{T} \frac{dT}{dz}$$

Assuming a normal geothermal gradient of 0.3K/m and applying the above equation to the LaBarge field at temperature, pressure and initial molar fraction of 410K, 440 bar and 0.14 respectively, we

can estimate the magnitude of the gravity and thermal diffusion.

$$\frac{gx_1}{RT} (\rho \bar{V}_1 - M_1) = \frac{9.81 \times 0.14}{8.314 \times 410} (592.9 \times (8.67 \times 10^{-5}) - 0.01604) \approx 1.4 \times 10^{-5}$$

$$K_T \frac{1}{T} \frac{dT}{dz} = \alpha x_1 x_2 \frac{1}{T} \frac{dT}{dz} = 0.1 \times 0.14 \times 0.86 \times \frac{1}{410} \times 0.3 \approx 1.0 \times 10^{-5}$$

Thus;

$$\frac{dx_1}{dz} = A[1.4 \times 10^{-5} + 1.0 \times 10^{-5}]$$

The above equation shows that thermal diffusion has a the same impact as gravity as the two terms are of the same magnitude.

If the value of α is increased to 0.25;

$$K_T \frac{1}{T} \frac{dT}{dz} = \alpha x_1 x_2 \frac{1}{T} \frac{dT}{dz} = 0.25 \times 0.14 \times 0.86 \times \frac{1}{410} \times 0.3 \approx 2.5 \times 10^{-5}$$

The thermal term will have a bigger impact than gravity. Thus as the thermal diffusion coefficient increases the impact of thermal diffusion will surpass that of gravity.

APPENDIX F: OVERVIEW OF STRUCTURE AND LITHOLOGY OF THE LABARGE FIELD

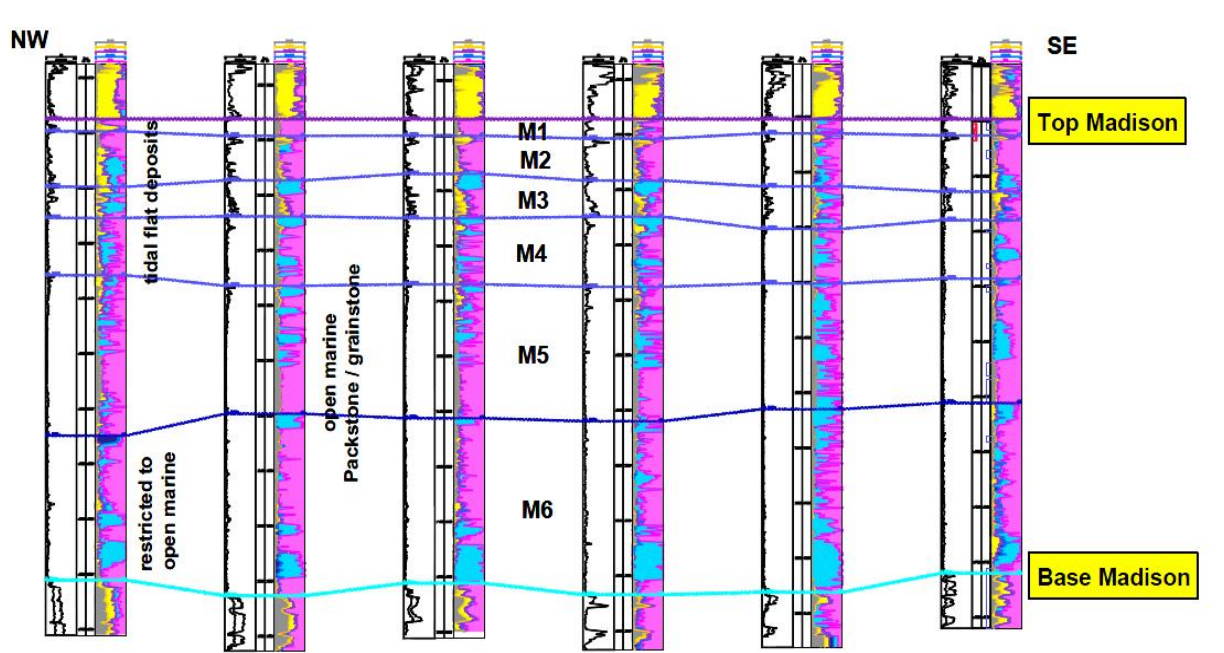


Figure F.1: Madison 3rd stratigraphic sequence framework. Gamma-Ray (on the left in thick lines) and % Lithology curves show distribution of limestone (blue), dolomite (pink), shale (grey) and anhydrite (purple). Adapted from Huang *et. al*, 2007.

From the figure above we can observe that the Gamma-Ray Logs have low readings through out the Madison formation and the % lithology plots show minimal amount of shale. This leads us to conclude that the Madison is a relatively clean formation with no barriers to flow.

APPENDIX G: COMPARISON OF THE RESULTS OBTAINED FROM ANALYTIC AND NUMERIC METHODS

In this section we shall compare the results obtained from the analytic and numeric method for a methane/undecane mixture (mixture used in Besong, 2010). We would use this to check the accuracy of the modifications made to the analytic solutions for the other initial conditions and to check if the computer program is working properly,; by reproducing the same results as Besong (2010)

INITIAL UNIFORM CONCENTRATION (x_{CH_4} of 0.6)

The results obtained from the numerical and analytic solution match. The maximum percentage error of was found to be 0.72%.

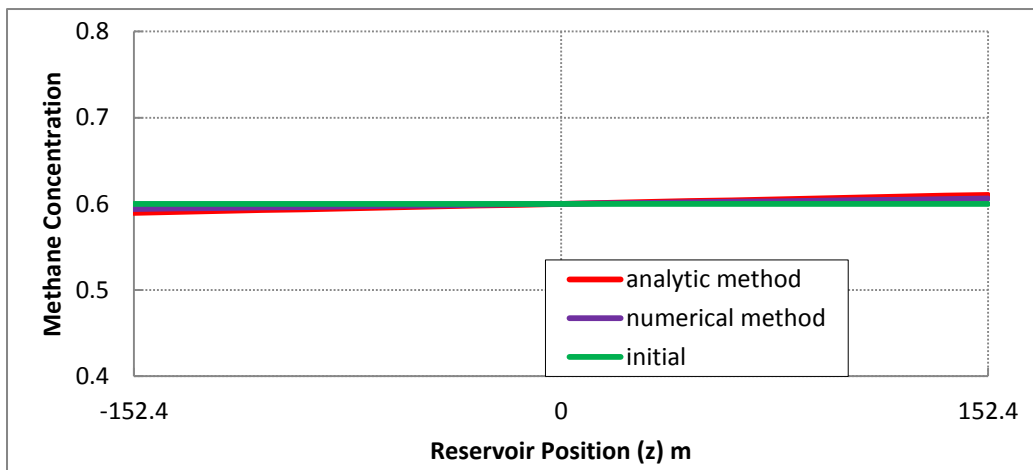


Figure G.1: Comparison of steady state profiles produced by the numerical and analytical methods for an ideal mixture of methane and undecane for a system with initial uniform concentration with depth.

STEP LIKE INITIAL CONCENTRATION DISTRIBUTION

Both species methane and undecane are split equally in the reservoir (occupy 50% each).

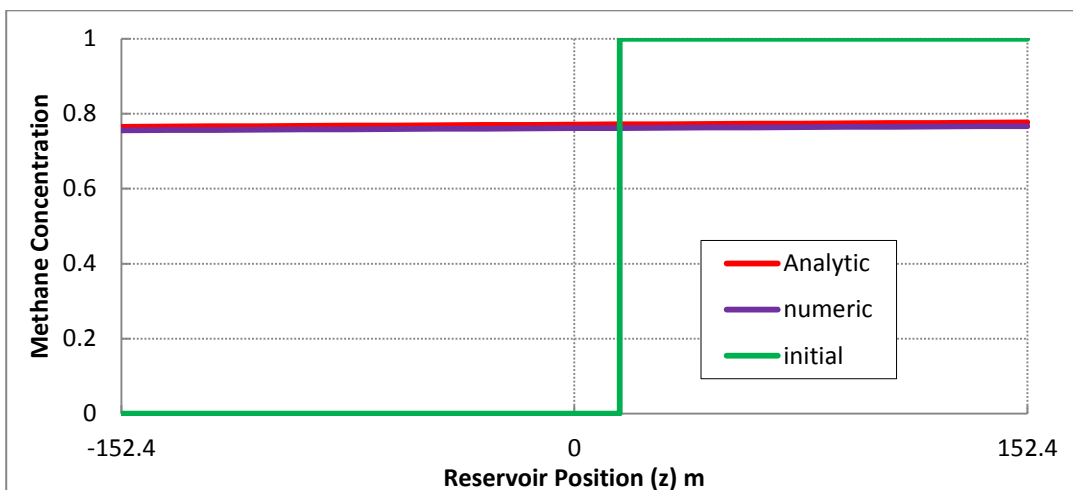


Figure G.2: Comparison of steady state profiles produced by the numerical and analytical methods

of an ideal mixture methane and undecane for a system with initial step function like concentration distribution.

The figure shows that the numerical and analytical methods show the same composition trend. The highest percentage difference between the two methods is 1.2%. These results also replicate the results in Fig 6.11e (Besong (2010)).

INITIAL UNIFORM GRADIENT

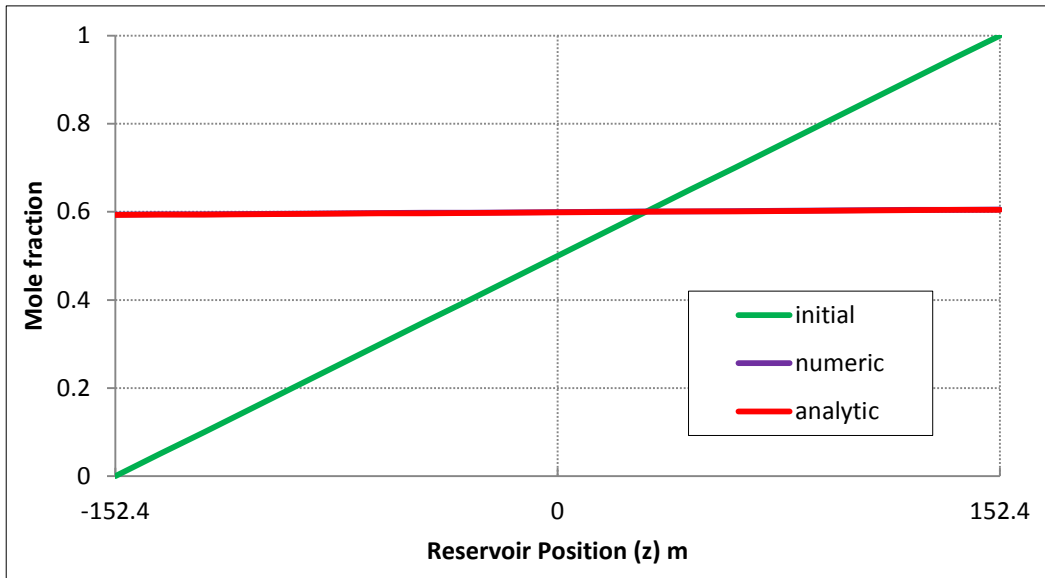


Figure G.3: Comparison between the numerical and analytical solution for an ideal mixture of methane and undecane in a system with a uniform mole fraction gradient with depth.

These two methods produce matching results with a maximum percentage error of 0.19%.

We can thus conclude that the two methods produce accurate results for the modelling of gravity and molecular diffusion for an Ideal mixture.