

SPE-174424-MS

Evaluation of Diffusion of Light Hydrocarbon Solvents in Bitumen

Franck Diedro, University of Calgary; Jonathan Bryan, Sergey Kryuchkov, and Apostolos Kantzas, University of Calgary, PERM Inc

Copyright 2015, Society of Petroleum Engineers

This paper was prepared for presentation at the SPE Canada Heavy Oil Technical Conference held in Calgary, Alberta, Canada, 9–11 June 2015.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

Solvent-based processes are often used as potential recovery agents in bitumen systems, with and without the addition of heat to the solvent. Solvents can sometimes be applied as a liquid phase, during SAGD start-up operations or processes aimed at developing injectivity into the oil. Light hydrocarbon liquids are traditionally tested for this application. Solvent injection may also occur in a vapour state and its objective is to reduce oil viscosity and improve mobility of bitumen under low temperatures $<100^{\circ}\text{C}$. In general, hydrocarbon solvents such as propane are often used for this application. The objective of this study is to conduct CT-based measurement of static mixing of bitumen and both liquid and vapour phase solvents, and to quantify some of the time-dependent changes that occur during solvent mixing with bitumen.

Diffusion experiments have been conducted with propane and DME (vapour phase) and with propane, DME, pentane and toluene (liquid phase) solvent systems. Solvents are mixed with medium viscosity Peace River bitumen and high viscosity Grosmont bitumen. The Tests are run under constant pressure and temperature, and Computer-Assisted Tomography (CT) is used to monitor mass transfer of solvent into oil as a function of time. The outcome of this study is measurements of mass transfer rates of solvent into oil, and the degree of oil phase swelling during the tests.

During solvent injection processes in the field, the rate of mixing is a key parameter that will help in deciding which solvent is optimal for different processes. This study focuses on the rate of solvent mixing with oil. In vapour phase solvent systems, the analysis of the CT images allows for an understanding of the impact of oil phase swelling on the effective rate of penetration of solvent into oil. Overall, the test data provided in this work demonstrates that DME mixes into oil faster than other solvents, and leads to more swelling in a vapour solvent-bitumen system. The analysis of CT data provides an understanding of concentration-dependent diffusion coefficients and limitations from predicting mass transfer using constant coefficients in liquid and vapour solvent systems.

Introduction

Solvent-based enhanced recovery of heavy oil and bitumen is gaining increased significance as a viable alternative or enhancement to steam. Many of the target oil properties for current and future development pose challenges to traditional SAGD operations. These fields tend to be smaller in size, thinner, or with other operational constraints such as reservoir depth or water-sensitive minerals. In addition, Alberta and

Saskatchewan contain significant remaining oil resources in post-CHOPS environments, where the presence of wormholes and non-thermal wellbores will make steam processes a challenge. Processes such as cyclic solvent injection (Ivory *et al.*, 2010), and variations of this process (Jiang *et al.*, 2013; Kristoff *et al.*, 2008) focus on the injection of vapour-phase solvents for heavy oil recovery. The concept behind these technologies is that solvent will mix with oil, thus reducing its viscosity and allowing for enhanced flow of the oil. Solvent is injected in a vapour phase, so that vapour will occupy the voidage left behind by either previous or current production of oil. Injection of vapour phase solvents is also intended to keep solvent content low enough in the oil such that issues such as asphaltene deposition will hopefully be reduced.

The challenge to vapour-phase solvent injection is the rate of mass transfer into the solvent is slow. For this reason, studies have focused recently on the addition of heat to these processes, with the goal of accelerating solvent mass transfer into oil (Nenniger and Dunn, 2008; Rassenfoss, 2012; Haghighat and Maini, 2013). Alternatively, new solvents can be considered that may have the potential for faster mass transfer into heavy oil and bitumen, even in the absence of heat.

Liquid solvents are often considered as additives to steam in thermal processes. In the absence of heat, their application in heavy oil and bitumen systems is more limited to reduction of oil saturation close to the production well in heterogeneous systems (Li and Mamora, 2010), and more recently to ideas of SAGD start-up enhancement (Ahmadloo and Yang, 2014). In these systems, the focus is on solvent penetration, still with the goal for mixing into oil and reducing its viscosity, but now for the purpose of increasing water mobility around injector and producer wells. Once again, the optimal solvent in this case is one that mixes quickly into oil, with minimal dropout of insoluble asphaltenes. Since liquid solvents are generally expensive, the goal of these systems is to use a solvent that has optimal mass transfer rates (i.e. fast mixing) to achieve solubility in oil with limited solvent volumes injected.

Hydrocarbon solvents are generally used for mass transfer into heavy oil and bitumen. Liquid solvents often include paraffins such as pentane or heptane, or aromatic solvents such as toluene to avoid precipitation of asphaltenes. Liquid propane may also be used in colder reservoirs, where it liquefies at low pressures. Propane, butane and carbon dioxide are the common options for hydrocarbon solvent vapour systems. The major challenge of using hydrocarbon solvents is their cost; with higher oil prices the costs accordingly rise for liquefied petroleum gas (LPG) products. Alternative solvents, which have similar mass transfer rates and solubility into these viscous oil systems, will be of considerable benefit to these processes. One such alternative is di-methyl ether (DME). DME (C_2H_6O) is often described as a “synthetic LPG”. This product can be manufactured directly from fossil fuels, or from renewable sources such as waste, pulp/paper mills and agricultural products (Taupy, 2007). World production of DME stands at over 5 million tons per year, with production coming mainly from China and Japan (IDA website, 2014). There are also plans and proposals to begin DME production in North America, so supply of this solvent could be possible in the volumes required for use in heavy oil and bitumen recovery, if its properties as a solvent prove to be sufficient.

DME has similar vapour pressure and density as LPG products such as propane, so transport and handling of this solvent will be similar to that of hydrocarbon solvents. Laboratory PVT studies with heavy oil have demonstrated the ability of DME to reduce oil viscosity by a similar fraction as propane, for a similar solvent content (Memon *et al.*, 2007). On the basis of its oil viscosity reduction, and on the basis of operational concerns, DME appears to be viable alternative to normal hydrocarbon solvents. This study focuses on mass transfer measurements of DME vs. other hydrocarbons, in order to understand the rate of DME addition compared to other more traditional solvents.

Measuring Solvent Mass Transfer Rates into Heavy Oil and Bitumen

Direct measurements of solvent mass transfer into oil are made by physically measuring solvent content within oil as a function of time. From these measurements, the diffusion coefficient of solvent into oil can

be found. Direct measurements are difficult and time consuming to conduct. As a result, mass transfer is generally measured indirectly: properties of oil-solvent systems are made over time, and changes in these properties reflect solvent mass transfer into oil.

One of the most common measurements of mass transfer into oil are pressure decay tests, wherein a heavy oil is placed in contact with vapour phase solvent at elevated pressures. As solvent moves into oil, pressure drops in the system and the rate of pressure drop is indicative of the solvent content within the oil. Various assumptions and boundary conditions are used to determine constant diffusion coefficients (Zhang *et al.*, 1998; Tharanivasan *et al.*, 2004; Sheikha *et al.*, 2005; Etniman *et al.*, 2010) and concentration-dependent diffusion coefficients (Upreti and Mehrotra, 2000; Ghaderi *et al.*, 2011). In these measurements, the initial solvent volume is fixed, so volume of remaining solvent drops as solvent moves into the oil. Other measurements that can be made for vapour-phase solvents include the pendant drop volume analysis technique (Yang and Gu, 2005), which can be used in constant solvent volume systems (i.e. where free solvent volume remains constant over time). These methods are not easy to apply in liquid solvent systems.

Density-based measurements are the other major technique used in the evaluation of solvent mass transfer into heavy oil and bitumen (Wen *et al.*, 2004; Salama and Kantzas, 2005; Luo and Kantzas, 2008; Guerrero-Aconcha and Kantzas, 2009; Song *et al.*, 2010). The technique applied to acquire system densities is computer tomography (CT), which outputs CT numbers that are directly proportional to density. By CT scanning of solvent-heavy oil systems over time, changes in CT numbers can be directly related to density changes within the system. The conversion of density to solvent concentration is made on the basis of assuming a linear relationship between density and solvent concentration:

$$C = \frac{\rho_o - \rho_{meas}}{\rho_o - \rho_s} \quad \text{Equation (1)}$$

Where

- C = concentration (volume fraction)
- ρ_o = density of heavy oil or bitumen
- ρ_{meas} = density of the heavy oil/solvent system at a given distance and time
- ρ_s = density of solvent.

In this approach the fundamental assumption in calculating solvent content within oil is this linear relationship between density and concentration. This infers an ideal mixing condition, meaning that solvent and oil mix with no change to the mixing of the two fluids. Certain works (Luo and Kantzas, 2008; Badamchi-Zadeh *et al.*, 2013) emphasize that oil volume may actually change with solvent addition, and this in turn will lead to changes in the solvent mass transfer rates within the oil. These volume changes have not been considered in this study, so the results presented allow for a comparison of different solvents against one another. Calculation of true diffusion rates will require proper PVT measurements to be made in each tested system.

Description of Tests and Systems

Figure 1 is a schematic of the testing apparatus that was used in this study. The oil/solvent systems are run in a horizontal cylindrical holder, with bitumen placed below the solvent during times of mixing. This system is gravity stable, and the cylindrical setup allows for CT images to be acquired without image artifacts caused by sharp corners, which would have occurred in a rectangular mixing cell. In each test, the mixing system is first partially filled with oil, and then the vessel is closed and put under vacuum. The initial CT scan is taken at this point, in order to tune the system for end point density values (oil and void space). Solvent is then placed into the system, and a CT scan is taken immediately as the zero time ($t = 0$) scan. CT images are acquired at periodic intervals, and changes in the oil and/or solvent density are taken to be indications of mass transfer and mixing of the fluids. Tests are stopped when the solvent has

penetrated completely through the oil; at this time the boundary conditions are no longer applicable for the solution of Fick's Law.

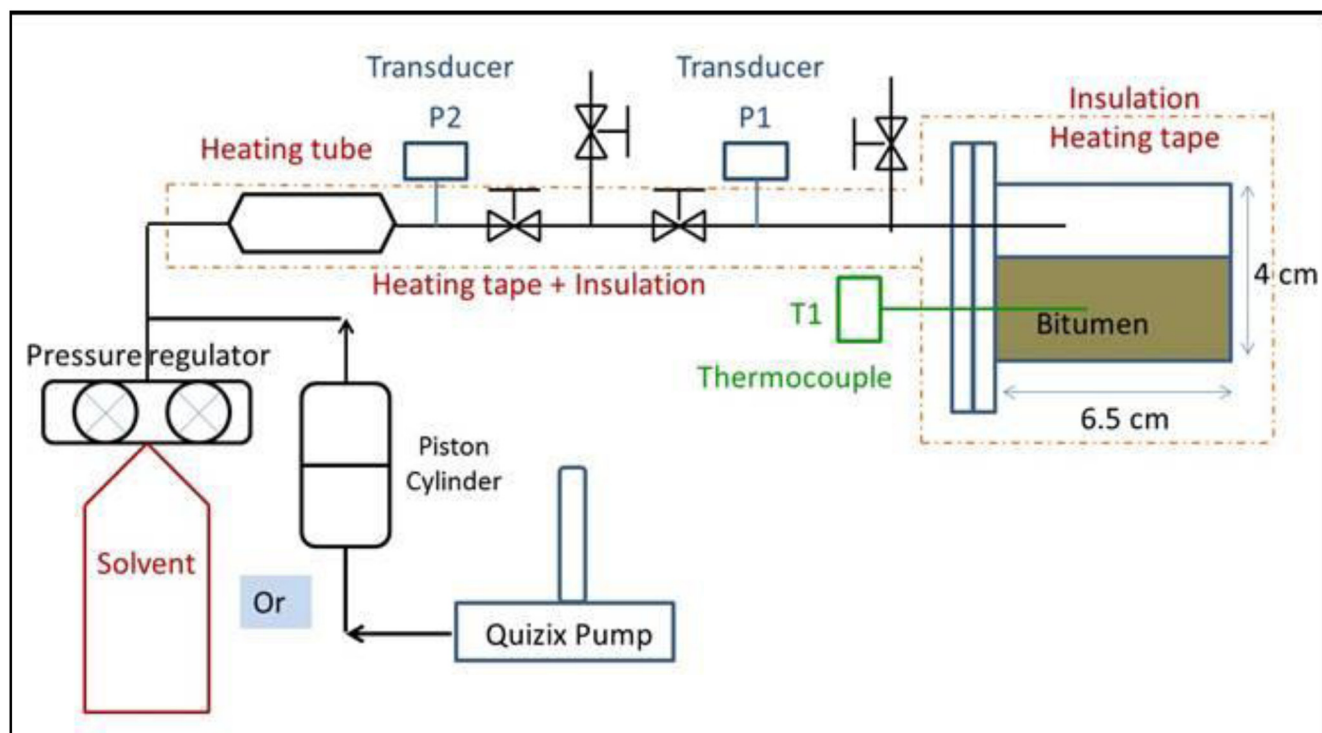


Figure 1—Schematic of Mass Transfer Test System

The two bitumen samples used in this study are from the Peace River (sand) and Grosmont (carbonate) systems. Figure 2 plots the viscosity of both bitumen samples as a function of temperature. At the test conditions of this study (22°C), the viscosity of Peace River bitumen is on the order of 55,000 mPa.s, compared to 12,000,000 mPa.s for Grosmont bitumen. Running tests on these two different bitumen samples allows for a comparison of solvent mass transfer rates in systems of very different initial oil viscosity.

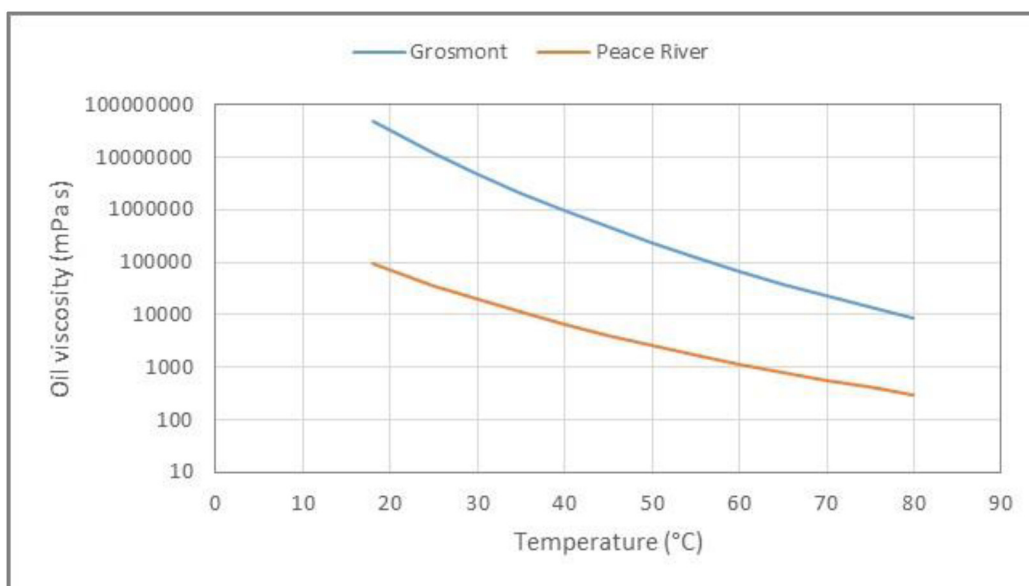


Figure 2—Viscosity of bitumen samples used in the solvent study

Liquid solvents tested are DME and propane (C3), with comparisons run against pentane (C5) and toluene. Table 1 lists the combinations of oils and solvents tested, and the solvent-oil ratios for each system. For most of the tests, solvent fraction is around 0.6. In the case of liquid solvents, which are infinitely soluble in bitumen, it is not necessary to keep solvent fraction exactly constant in each system in order for them to be compared. So long as there is a sufficiently large solvent fraction such that free solvent will be present during the time of the test, calculations of mass transfer can still be made.

Table 1—Liquid Solvent Test Systems Studied

Oil	Solvent	Oil (g)	Solvent (g)	Oil (cm ³)	Solvent (cm ³)	Solvent fraction
Peace River	DME	30.9	33.8	30.5	51.2	0.63
Peace River	Pentane	30.7	32.2	30.3	51.3	0.63
Peace River	Toluene	31.5	43.5	31.1	50.5	0.62
Peace River	Propane	44.2	21.2	43.7	38.0	0.47
Grosmont	DME	35.1	31.1	34.6	47.1	0.58
Grosmont	Pentane	28.9	33.3	28.5	53.2	0.65
Grosmont	Toluene	30.9	44.0	30.5	51.2	0.63
Grosmont	Propane	35.1	26.3	34.6	47.1	0.58

Vapour-phase solvents are DME and propane (C3), which were again measured in both bitumen systems. The amount of solvent present depends on the pressure of each system, so in Table 3 solvent volumes are reported both at the system pressure and at standard (atmospheric) pressure conditions. The pressures for DME and propane are different; the goal was to mix solvent into oil at pressures that are similar to, but slightly lower than, saturation pressure of solvent at 22°C. This was by design, to maintain the solvents in a vapour state but maximize solubility into oil. DME was run at a lower pressure than propane because its vapour pressure is lower than that of propane. For solvent-based enhanced recovery processes, this is also a positive note for DME, since it will be easier to maintain the solvent in an injected

vapour state during field operations. Pressures were set to be close to the saturation pressure of both solvents, but it should be emphasized that systems are not compared at the same ratio of P/P_{sat} .

Table 2—Average Diffusion Coefficient Values for Liquid Solvents in Bitumen

	Average D (cm ² /s)		D/D_{DME}	
	Peace River	Grosmont	Peace River	Grosmont
DME	4.93E-06	2.40E-06	1	1
C3	3.99E-06	3.02E-07	0.81	0.13
C5	2.93E-06	1.21E-06	0.59	0.51
Toluene	1.71E-06	1.85E-06	0.35	0.77

Table 3—Vapour Solvent Test Systems Studied

Temperature	Oil	Solvent	Pressure (kPaa)	Oil Vol (cm ³)	Solvent (cm ³)	Solvent Vol @ 1 atm (cm ³)
22	Peace River	DME	377	29.5	52.2	194.2
22	Peace River	Propane	722	31.5	50.1	357.2
22	Grosmont	DME	446	35.6	46.0	202.6
20	Grosmont	Propane	722	41.8	39.8814	284.1

Measurements in Liquid Solvent Systems

As discussed previously, CT-based measurements of oil and solvent systems rely on a linear conversion of CT numbers into density. This was achieved by running standard samples of known density in the same mixing cell environment as the tested liquids, and building the CT-density calibration using these samples. Figure 3 then shows the measured CT density profiles of a liquid solvent-bitumen system over time, as solvent mixes into oil. The original oil-solvent interface is set ($x=0$). Positive values of x are the oil phase, and negative values of x are the solvent. Over time, Figure 3 shows that solvent mixing into oil (positive x -values) leads to reductions in density of the oil-rich phase. Correspondingly, oil mixing into liquid solvent (negative x -values) results in density of the solvent-rich phase increasing with time.

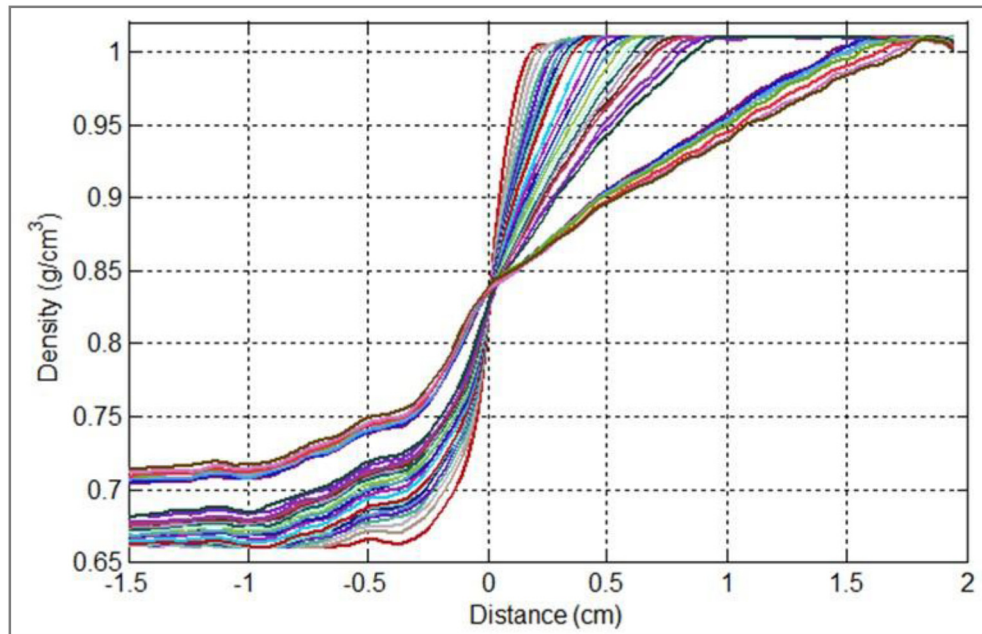


Figure 3—Liquid solvent-bitumen density changes as solvent mixes into oil

Density was converted linearly into concentration, following Equation (1). Figure 4 plots solvent concentration for several mixing times, for liquid DME diffusing into Peace River bitumen. Bitumen content within the solvent-rich phase increases with time, and so does solvent content within the oil-rich phase. After two days of mixing, it can be observed that solvent has propagated throughout the oil, and oil content is now less than 1 at the outlet end of the mixing cell ($x = 2$ cm). The simple solution of Fick's Law of mass transfer requires an infinite boundary condition (i.e. solvent concentration = 0 at $x \rightarrow \infty$). Therefore, by the mixing time of two days, this assumption is no longer met and mass transfer should only be calculated from earlier times.

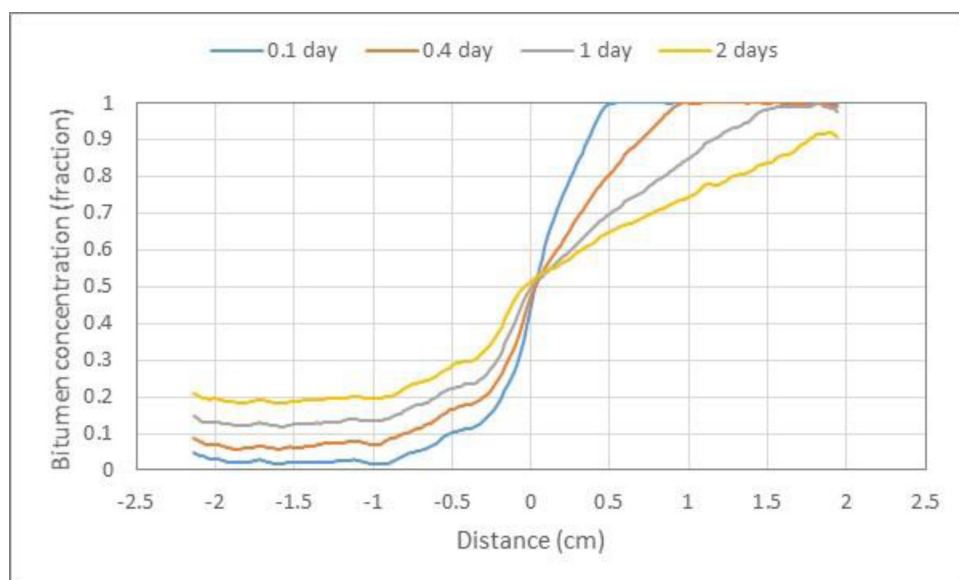


Figure 4—Concentration of liquid solvent into bitumen as a function of mixing time

Four liquid solvents were tested: DME, propane (C3), pentane (C5) and toluene. Their penetration profiles into Peace River bitumen are compared all at 24 hrs of static mixing time in Figure 5. Figure 6 shows the same solvent penetration profiles, also at 24 hrs of static mixing time, but now into the more viscous Grosmont bitumen. Two observations can be made from these two figures. The first observation is that, for either bitumen, DME has progressed further than any of the other liquid solvents tested. This indicates that mass transfer rates are highest for DME, which makes it a good solvent. The second observation is that, for the same static mixing time, solvent penetration depths are further for Peace River bitumen compared to Grosmont bitumen. This is an indication that mass transfer rates are faster in less viscous oils, which is an expected result. This result is shown more clearly in Figure 7, which compares DME content in both bitumen samples at two static mixing times: 0.1 days a 1 day of mixing. Solvent has clearly penetrated further in the lower viscosity oil. This means that diffusion coefficient is different for different oil systems, and mass transfer is faster in lower viscosity oils.

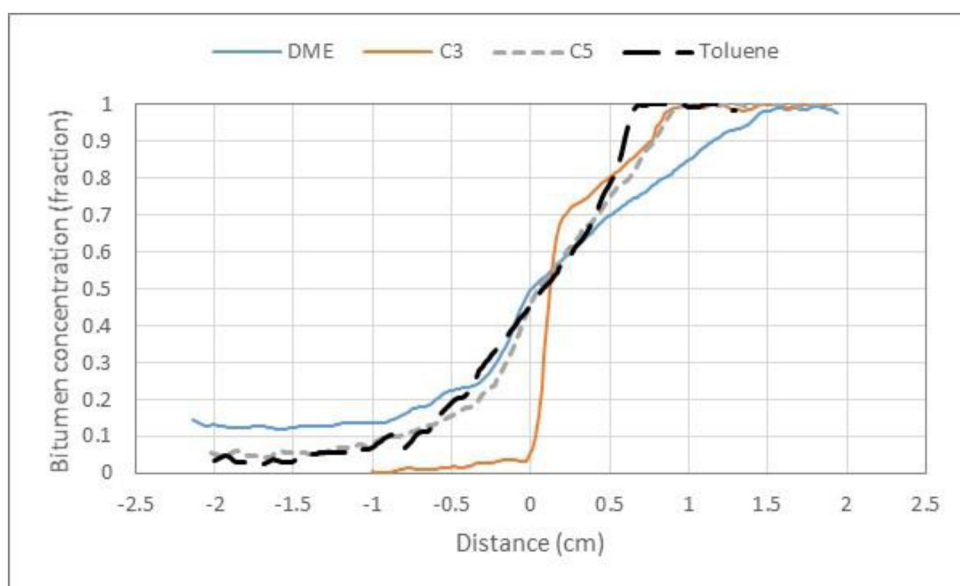


Figure 5—Mass transfer of different liquid solvents into Peace River bitumen (24 hrs)

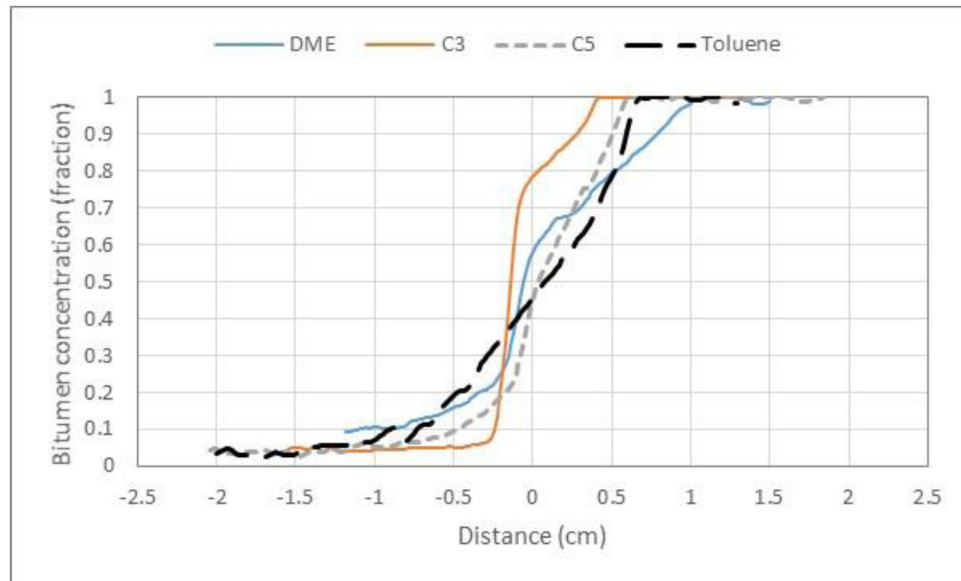


Figure 6—Mass transfer of different liquid solvents into Grosmont bitumen (24 hrs)

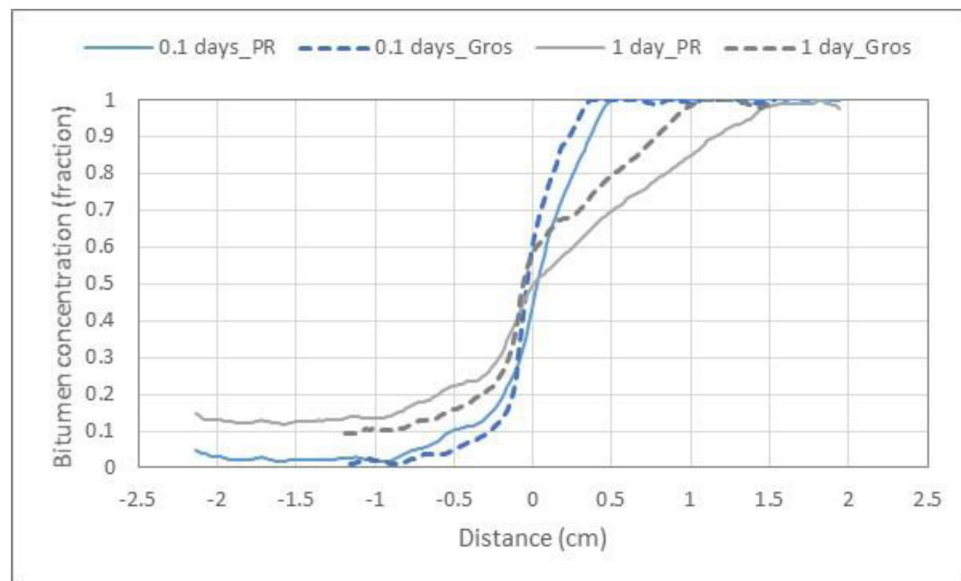


Figure 7—Mass transfer of liquid solvent (DME) into Peace River vs. Grosmont bitumen

Diffusion coefficients were calculated using the slopes and intercepts method (Sarafianos, 1986; Guerrero-Aconcha *et al.*, 2008). The output from this solution technique is the diffusion coefficient of solvent into bitumen, which is expressed as a function of solvent content. In Figure 8, concentration-dependent diffusion coefficients are plotted for all four solvents in Peace River bitumen, while Figure 9 shows the calculated diffusion coefficients in Grosmont bitumen. Overall, diffusion coefficients for the more viscous bitumen (Grosmont) appear to be lower than that of the less viscous Peace River sample. This is shown more clearly in Figure 10, which compares the diffusion coefficient profiles for liquid DME in both Peace River and Grosmont bitumen samples. As expected from the observations of lower solvent penetration distances during the test, diffusion is slower in the more viscous oil.

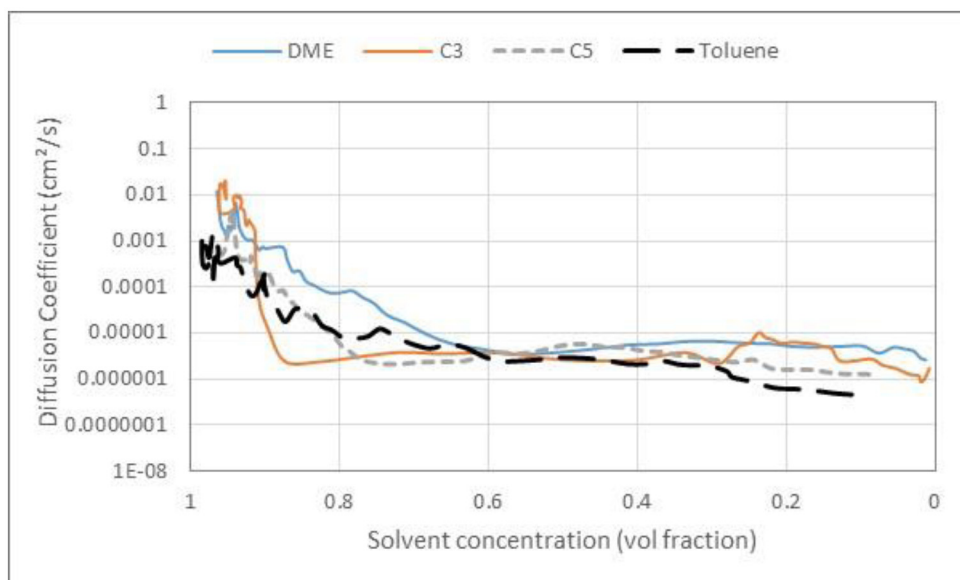


Figure 8—Slopes and Intercepts diffusion coefficient of various liquid solvents in Peace River bitumen

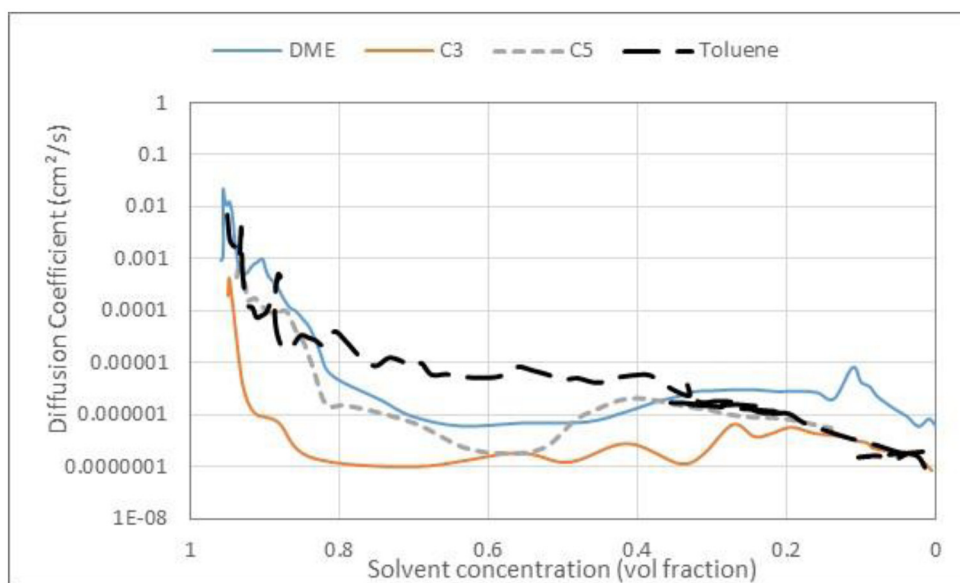


Figure 9—Slopes and Intercepts diffusion coefficient of various liquid solvents in Grosmont bitumen

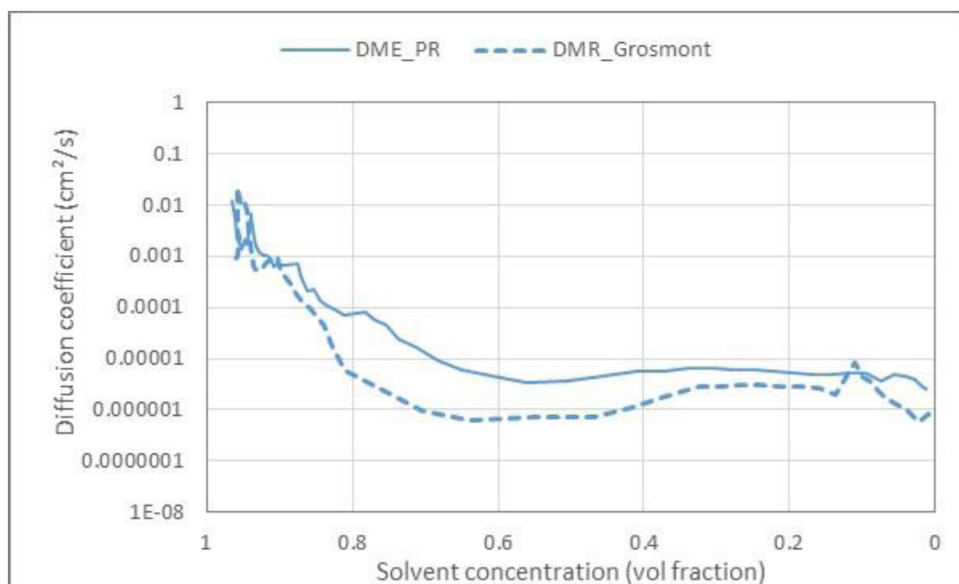


Figure 10—Slopes and Intercepts diffusion coefficient of liquid DME mixed with Peace River and Grosmont bitumen

In all the samples, diffusion of solvent into oil occurs at the lower solvent fractions (i.e. solvent concentration < 0.5). The higher solvent content portion of all systems is the mass transfer of bitumen into the free solvent phase. Here viscosity is much lower and accordingly diffusion coefficient values are also higher. These figures show that diffusion coefficient is not only a function of concentration, but also it is a function of the viscosity of the liquid-solvent mixture.

An interesting observation from Figures 8 to 10 is that, in the bitumen-rich portion of the system (i.e. for solvent concentration < 0.5), the values for diffusion coefficient appear to be relatively constant, at least on the log scales used for plotting these systems. The average (mean) diffusion coefficient is found for each system within this low solvent concentration range, and Table 2 lists these average values. Clearly, mean diffusion coefficient values are consistently smaller for Grosmont bitumen, compared to Peace River bitumen. But what is also output on this table is the ratio of diffusion of each liquid solvent compared to that of liquid DME. All ratios are less than one, indicating that DME has the highest mean diffusion coefficient rate of any of the tested liquid solvent systems. This verifies the observations of the furthest solvent penetration distances for DME, at any measured time.

The results from Figures 8 to 10 show that diffusion coefficient is a function of solvent concentration, but the dependence on solvent concentration is perhaps lower within the oil-rich phase. To test the significance of the concentration dependence, Fick's Law was solved for DME into Peace River bitumen assuming the fixed value from Table 2, and the resulting concentration profile was plotted and compared to the measured values from the actual test. Figure 11 shows this comparison for two times: 0.1 days and 1 day of static mixing. Bitumen concentration ($1 - \text{solvent concentration}$) is plotted in this figure, since the mass transfer is occurring within the oil-rich phase. At the solvent-oil interface the maximum solvent concentration is used (0.5), and as the solvent penetrates into the oil, its concentration decreases and accordingly bitumen concentration increases. Overall, the constant diffusion coefficient results are qualitatively similar to the measured values measured in the laboratory study. On a pragmatic basis, it seems that constant diffusion coefficients can be used to get a reasonable prediction of solvent penetration distance into oil for any given mixing time.

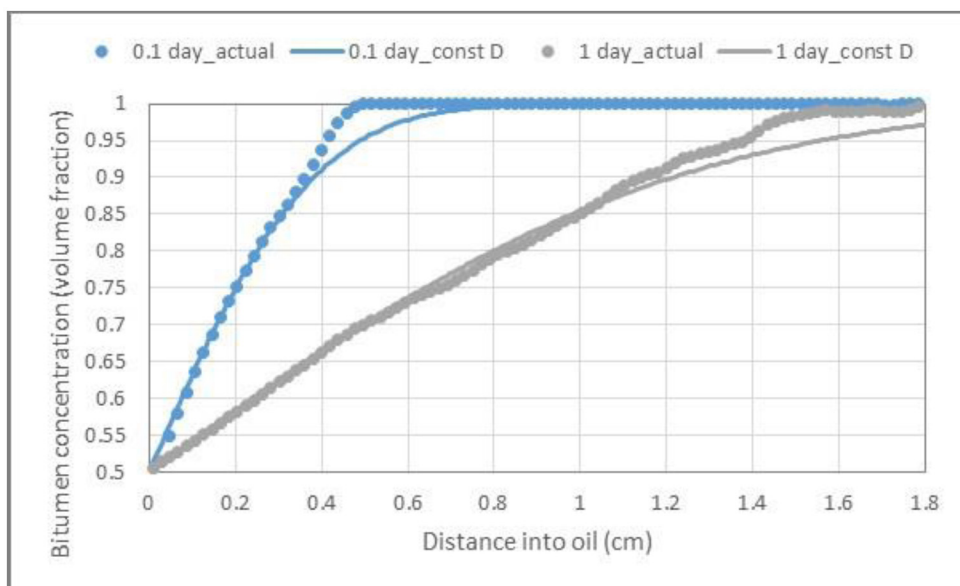


Figure 11—Measured liquid solvent penetration rate (DME in Peace River bitumen) - comparison against predicted profile with constant diffusion coefficient

The biggest difference between the measured profiles and the predicted profiles using constant diffusion coefficients occurs at the edge of the solvent penetration front. The constant diffusion assumption leads to solvent content gradually dropping to zero as solvent penetrates further into the oil. This is not what is observed in the actual liquid systems. In fact [Figures 4 to 7](#) all show solvent penetration profiles that appear to be straight lines of solvent mixing into oil. This is a key observation, because it has physical significance for understanding the means why which mass transfer occurs in these viscous oil systems. Bitumen at high concentrations is so viscous that the oil acts almost like a wall, impenetrable to solvent. When there is some solvent already present mixed into oil, then mass transfer can occur. But when solvent content becomes too low, the bitumen itself seems to act almost like a barrier to further mass transfer. This is conceptually similar to a solid being washed with a solvent, and only the part that is washed can be represented by mass transfer and Fick's Law solutions.

The next question to be answered was whether the slopes and intercepts model (concentration-dependent diffusion coefficient) does a better job of capturing the physics of the system. [Figure 12](#) plots the initial solvent-oil interface at (time = 0), and also the measured solvent penetration profile at a later time. The concentration-dependent diffusion coefficient was calculated using the slopes and intercepts analytical method, and was input into a model mass of mass transfer in a finite element numerical simulator (COMSOL). The measured (experimental) solvent concentration profile is shown as blue crosses in [Figure 12](#), and the predicted solvent concentration profile, using the variable diffusion coefficient, is plotted as a solid orange line. The slopes and intercepts model captures the overall penetration rate of solvent into oil, but again at the edge of the mixing zone (i.e. at very low solvent content) the slopes and intercepts model values also over-estimate solvent penetration, and show a gradual mixing into oil, compared to the measured straight line solvent content profile.

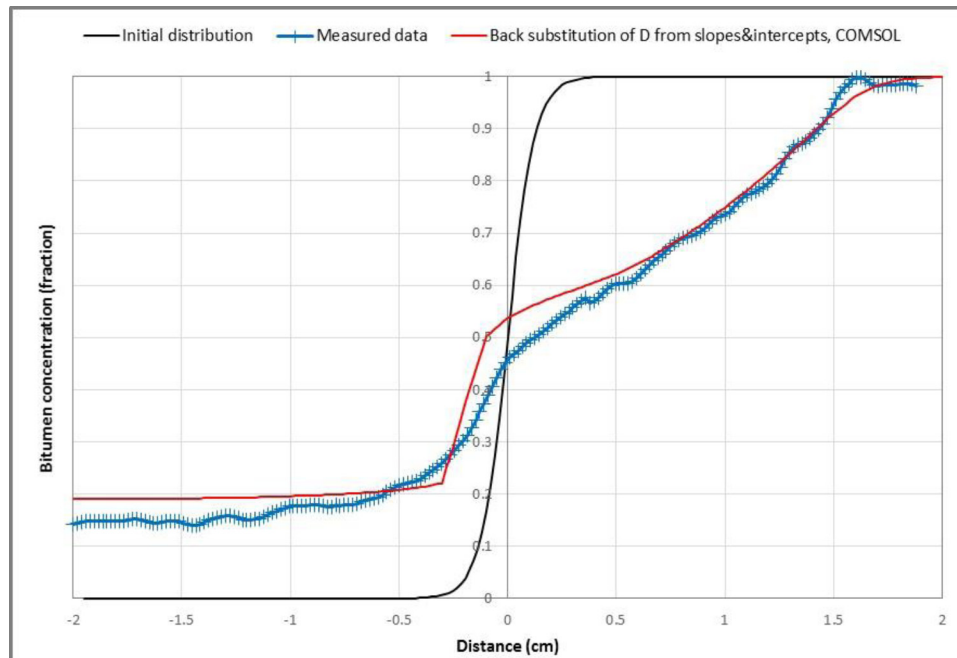


Figure 12—Check of Slopes and Intercepts Method ability to model linear liquid solvent penetration into bitumen

It appears that both models of diffusion of solvent into oil have difficulty in capturing the shape of the solvent penetration profile as solvent content approaches zero. In order to properly capture the measured system response, a different model must be used, which allows for solvent diffusivity to become zero when solvent content is equal to zero. This model is the focus of ongoing work. The other parameter of interest is the shape of the diffusion coefficient at the oil-solvent interface (i.e. at $x = 0$). Figure 12 clearly shows that, at the interface, the solvent concentration drops abruptly. The only way to capture this response is to have the diffusion coefficient decrease at the interface, and later increase again within the solvent-rich phase. This is what is predicted in the slopes and intercepts model outputs (Figures 8 to 10). The physical reason for this behavior is also the focus of ongoing studies.

Measurements in Vapour Solvent Systems

As discussed previously, liquid solvent systems would be used for near-wellbore applications such as improving mobility of oil close to wells, or accelerating SAGD startup operations. For actual non-thermal solvent EOR applications, solvents will always be injected as a vapour phase (i.e. at pressures less than the saturation pressure of the solvent at the reservoir temperature). Vapour solvents are required to fill the voidage from previous production and contact fresh oil. DME and propane vapour systems are compared in this study, once again in Peace River and Grosmont bitumen. Table 3 lists the volumes of oil and solvent used in the various test systems.

As with the liquid solvent systems, mass transfer was measured via CT measurements of density, which would decrease as solvent was dissolved into oil. Figure 13 plots measured density profiles that are acquired over time. Density was converted into solvent content using the linear assumption of Equation (1), and Figure 14 shows how solvent concentration increases within the oil phase with increased diffusion times.

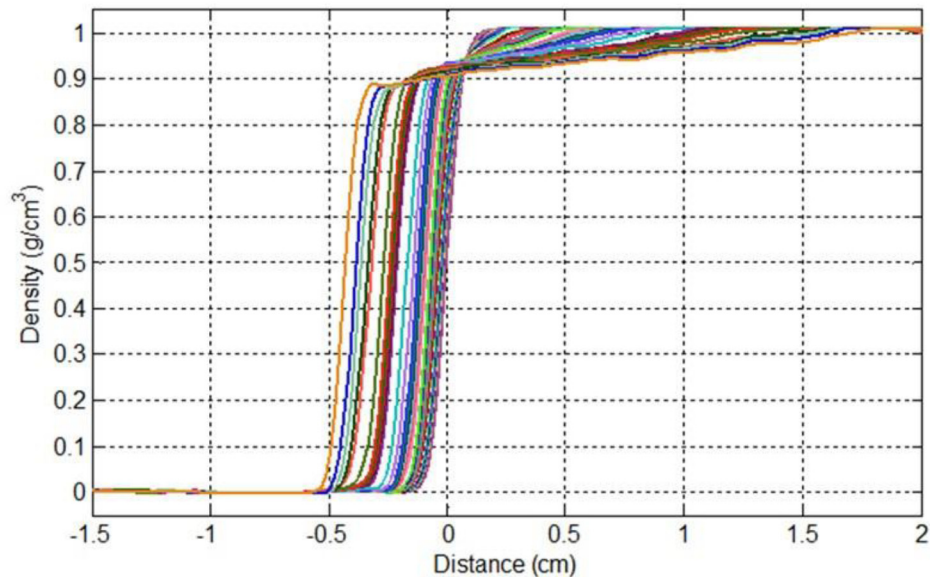


Figure 13—Vapour solvent-bitumen density changes as solvent diffuses into oil and oil phase swells

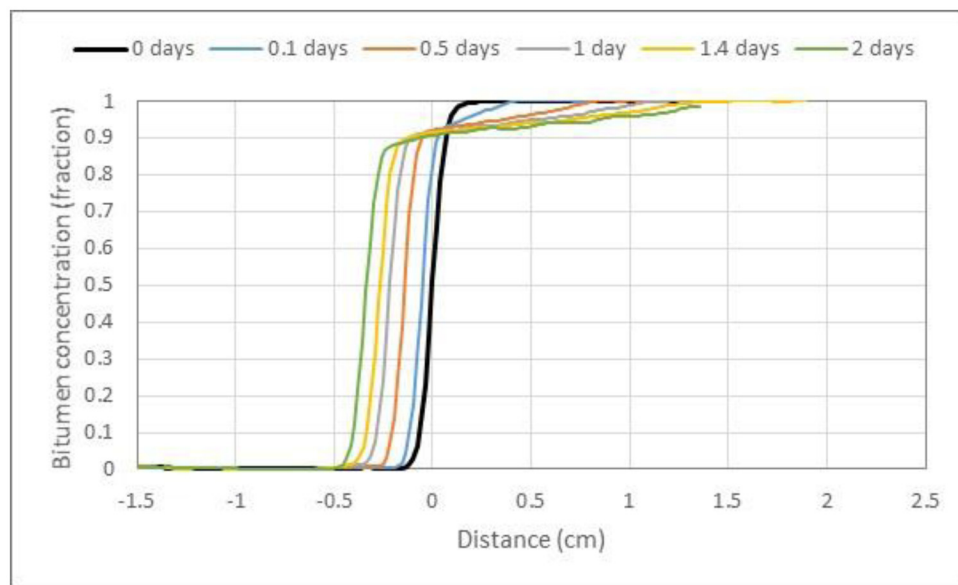


Figure 14—Concentration of vapour solvent into bitumen as a function of mixing time

In Figure 14, the initial solvent-oil interface is shown as the bold black curve, and the interface is set at distance $x = 0$. Several observations can be made from the plot of solvent concentration in oil at later times. The first is that, as solvent moves into the oil (i.e. positive values of x), oil density decreases and this corresponds to increased solvent content within the oil. Solvent penetration distance increases with time, and follows the same straight-line behaviour that was previously observed in the liquid solvent systems. Note that this straight-line behaviour has not been observed for lower viscosity heavy oils (Song *et al.*, 2010); in those oils solvent penetration followed the “s-shape” curve that is expected from diffusion-based mass transfer. Therefore, the observation of these straight-line penetration profiles, and the explanation of bitumen acting almost like a solid barrier to solvent at low solvent content, is only for these highly viscous bitumens.

Another observation that can be made from Figure 14 is that, as diffusion time increases, the oil-solvent interface moves, and the oil phase is essentially growing in size. This is the phenomenon of oil phase swelling, which can be an important EOR mechanism in solvent processes. The degree to which different solvents lead to swelling in oil will be another means of comparing vapour solvents; higher swelling will tend to push the diluted oil towards the production well. This was observed only in the vapor solvents.

The final observation that can be made from the experimental measurements is that, over time, the solvent content at the edge of the oil-solvent interface becomes constant. In liquid solvent systems, the system equilibrates to equal concentrations (i.e. solvent concentration of 0.5 at the interface). For vapour solvents, the final value of concentration at the interface is the solvent solubility within the oil. Table 4 lists the measured solubility values for DME and propane in the two bitumen samples. In either bitumen, the solubility of DME is higher compared to that of propane, even for cases where DME has lower P/P_{sat} compared to propane. Past laboratory studies (Memon *et al.*, 2010) have shown that DME and propane can reduce oil viscosity by a similar ratio, for a similar solvent content present in the oil. The fact that DME has higher solubility compared to propane means that, in theory, this solvent may be able to reduce viscosity more effectively than propane vapour.

Table 4—Solubility of Different Vapour Solvents in Oil (22°C)

Oil	Solvent	Pressure (kPaa)	P/P _{sat}	C0 (volume fraction)
PRB	DME	377	0.70	0.14
PRB	Propane	722	0.82	0.08
Grosmont	DME	446	0.82	0.15
Grosmont	Propane	722	0.82	0.05

Figures 15 and 16 compare the solvent penetration of DME and propane into Peace River bitumen and Grosmont bitumen, respectively. Both figures show the penetration profiles that were observed after 24 hrs of mixing at constant system pressures. Clearly mass transfer is once again faster in the less viscous oil, which was also observed in the liquid solvent systems. In comparing the response of the systems to DME vs. propane, for the same mixing times DME has penetrated further than propane into the oil and furthermore swelling appears to be higher with DME as well.

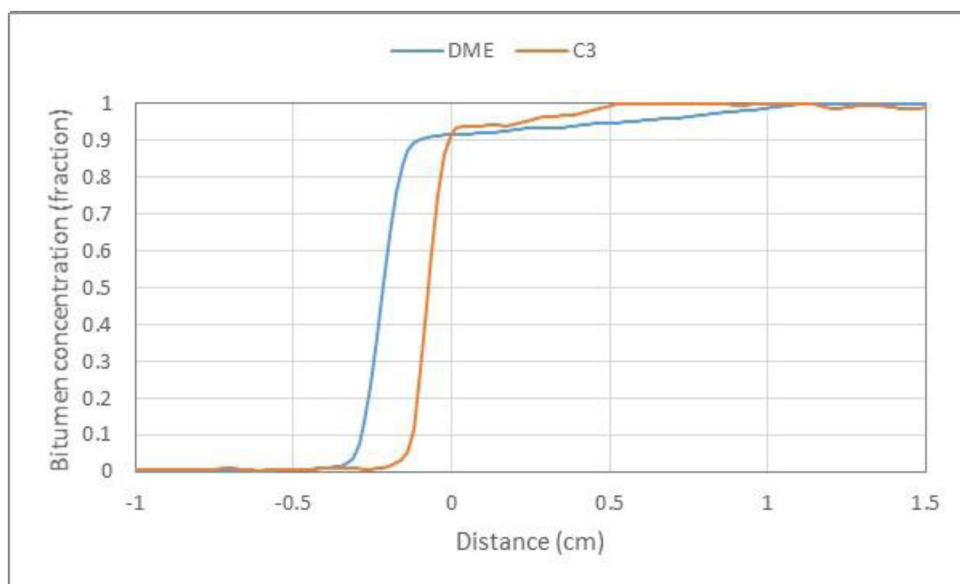


Figure 15—Mass transfer of different vapour solvents into Peace River bitumen (24 hrs)

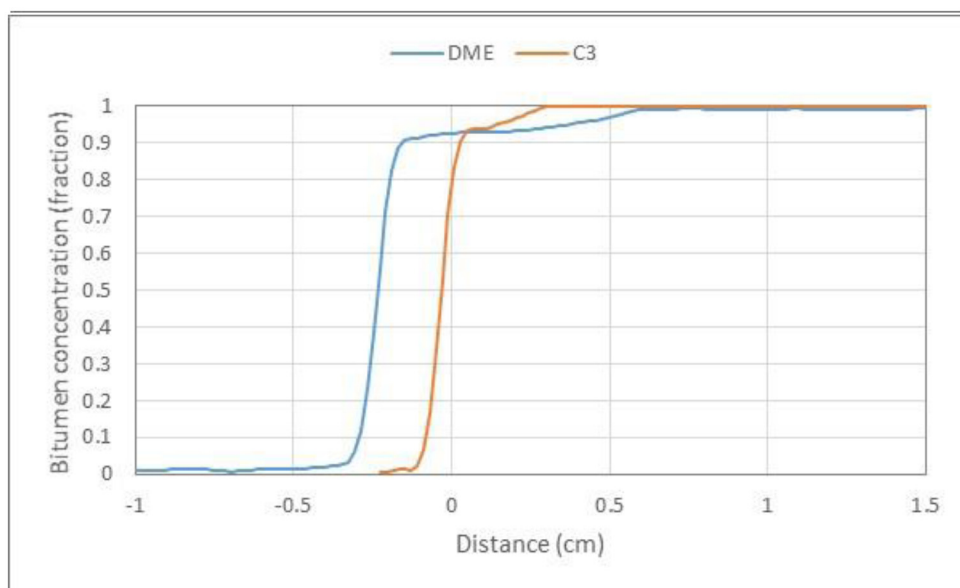


Figure 16—Mass transfer of different vapour solvents into Grosmont bitumen (24 hrs)

Diffusion coefficients were calculated for the solvent that is within the oil-rich phase. Figure 17 plots the profiles as a function of solvent concentration within the oil. Note that concentrations within the oil are much lower than for the liquid solvent systems (Figures 7 and 8). Once again, within the log scale used to plot these profiles, it appears that an approximation of a constant diffusion coefficient may be valid to model the solvent penetration rate. Table 5 lists the average values for diffusion of DME and propane in both bitumen samples. As was observed from the solvent penetration distances, DME has a higher mean diffusion rate compared to propane. The average value of either solvent is also higher in Peace River bitumen compared to Grosmont, indicating that there is a viscosity influence on diffusivity as well. This was also observed in the liquid solvent systems.

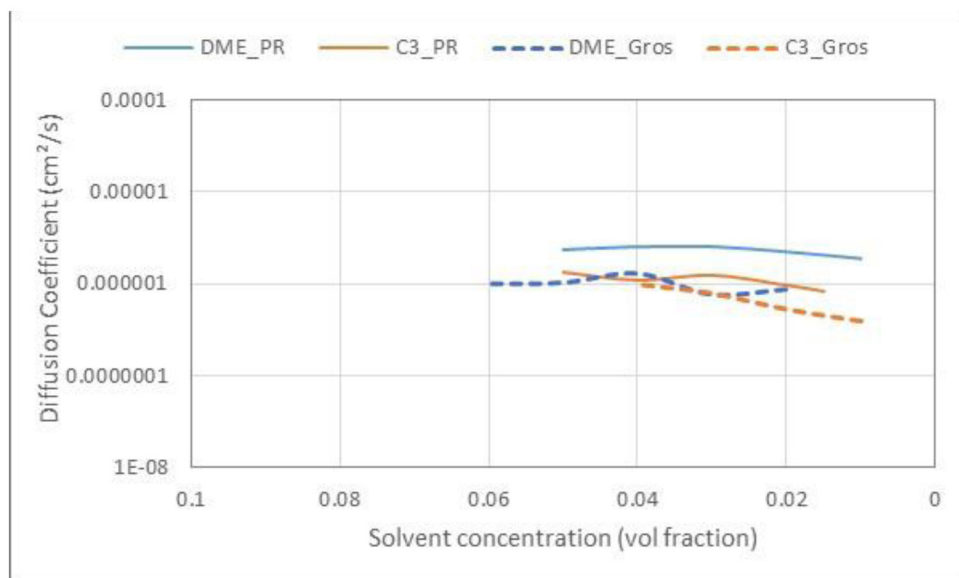


Figure 17—Concentration dependent diffusion coefficients of vapour phase solvents into bitumen

Table 5—Average Diffusion Coefficient Values for Vapour Solvents in Bitumen

	Average D (cm ² /s)		D/D_{DME}	
	Peace River	Grosmont	Peace River	Grosmont
DME	2.31E-06	8.97E-07	1	1
Propane	1.10E-06	6.80E-07	0.47	0.76

The constant diffusion coefficient assumption was tested for its ability to model the solvent mass transfer rate into the oil. This was done by taking the constant value from Table 5 and modeling simple diffusion mass transfer (Fick's Law) for vapour solvents mixing into oil. This result is shown in Figure 18. The measured initial interface (time = 0) is shown as the solid black line in this figure. Experimental profiles at 1 day and 3 days of mixing are plotted as points, and the predictions for these same times are shown as solid lines. The solution to Fick's Law assumes that the solvent-oil interface is always at ($x = 0$), and solvent penetrates into the oil beyond this point. This solution does not take into account volume changes in the oil phase due to swelling. For this reason, the simple Fick's Law solution (constant diffusion coefficient) looks quite different from the measured profiles in Figure 18.

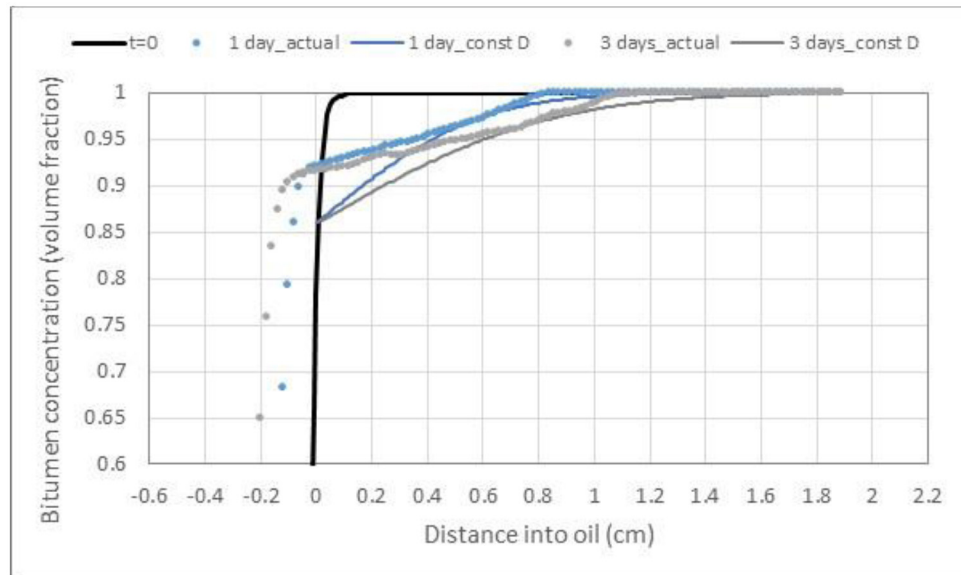


Figure 18—Measured vapour solvent penetration rate (DME in Peace River bitumen) - comparison against predicted profile with constant diffusion coefficient

The effect of swelling was accounted for by manually moving the interface location to negative values of x . Figure 19 compares the solvent penetration from these new adjusted interface locations. Even after accounting for swelling, the shapes of the modeled mass transfer are different from what was actually measured in this test. The reason for this is that Fick's law assumes that the interface is already saturated with solvent (C_0 values from Table 4). In reality, it takes some time even for the interface to become saturated, so the boundary condition for modeling vapour-phase solvent flow needs to be changed to reflect this state.

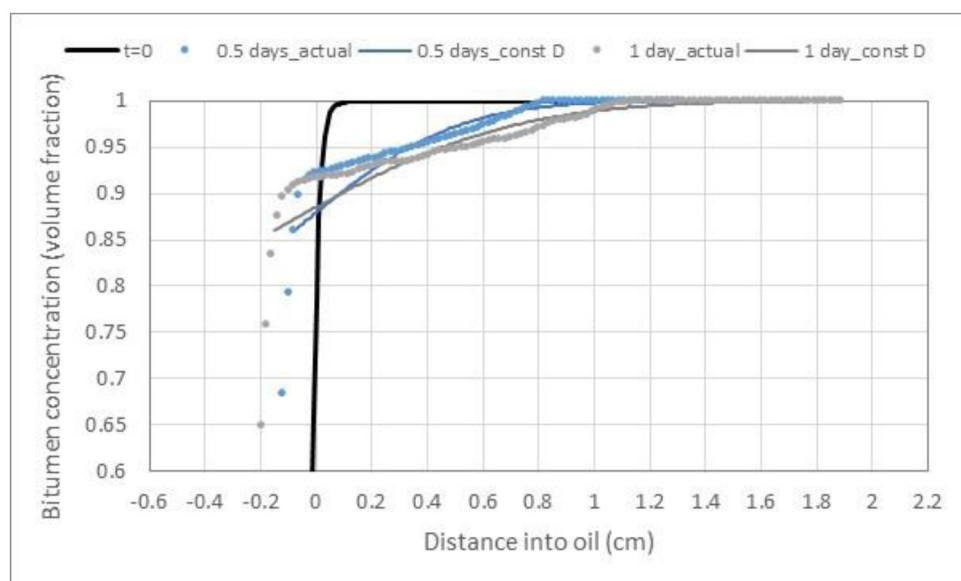


Figure 19—Measured vs. predicted vapour solvent penetration rates (DME in Peace River bitumen) - manual adjustment for swelling

The other observation that can be made from Figure 19 is that the constant diffusion coefficient approach tends to overestimate solvent penetration distance into the oil, particularly at the edge of the

solvent penetration (i.e. at very low solvent content). The linear solution to the diffusion equation once again does not represent the straight-line profiles of solvent within the oil. In order to properly capture the physics of these systems, a new model needs to be developed that accounts for the diffusion of solvent becoming zero when solvent content in the oil is zero as well.

The observations of solvent mixing into bitumen in the vapour phase clearly show the importance of oil phase swelling due to solvent addition. Swelling of the oil was quantified by measuring the oil phase volume as a function of time from CT images, and comparing this volume to the initial oil volume at (time = 0). Figure 20 plots the oil phase swelling fraction for DME and propane in both tested bitumen samples. Swelling is larger in the less viscous Peace River bitumen, compared to Grosmont bitumen. This is again most likely related to the slower mass transfer into the more viscous oil. The most significant observation from this figure, however, is that DME leads to significantly more swelling of bitumen compared to propane. Not only is mass transfer and overall solubility higher for this solvent, but swelling is also larger.

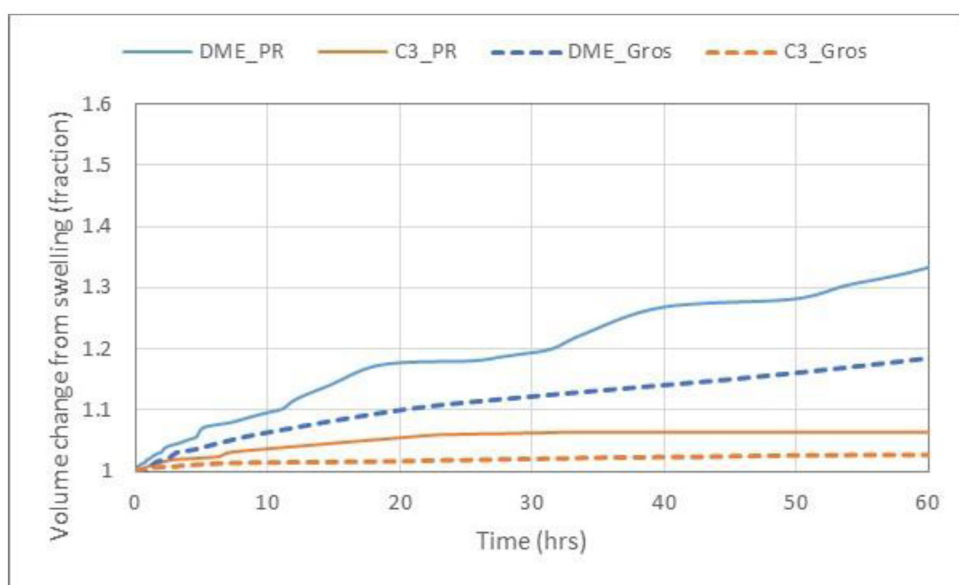


Figure 20—Volume change (swelling) of Peace River and Grosmont bitumen due to mixing with DME and propane vapour solvents

Conclusions

Di-methyl ether (DME) has potential for use as a non-thermal solvent in heavy oil and bitumen systems. When compared against other liquid solvents (propane, pentane and toluene), DME consistently shows the highest mass transfer rates. As a vapour phase solvent compared to propane gas, DME exhibits higher maximum solubility in oil, faster mass transfer, and also considerably more swelling of the oil phase. This study does not consider the economics of acquiring DME supply and parameters such as asphaltene dropout in liquids, or the ability of the solvent to leave solution with oil in the vapour phase (for solvent recovery and recycling). Therefore, what is presented in this study is not a complete picture of the validity of DME as a non-thermal solvent. However, on the basis of mass transfer metric alone, DME could be an exciting alternative to other hydrocarbon solvents.

Diffusion coefficients were calculated as a function of solvent concentration in this study. Average values of these diffusion terms were also found, and tested to see if these constant values could be used to predict solvent mass transfer rates into oil. This approach was followed for both liquid and vapour solvent systems. It was observed that, in general, the average (constant) values of diffusion were able to predict solvent penetration rates into bitumen in liquid systems. For vapour systems, the saturation

condition of the oil interface happens gradually with time, so the solution to the diffusion equation requires a different boundary condition.

Predictions of mass transfer rates, using either fixed or variable diffusion coefficients, would tend to slightly over-estimate the final distance of solvent moving into oil at low solvent concentrations. The simplified constant diffusion values can be used to get a relative prediction of solvent distances with time, but they do not properly capture the true physics of the solvent penetration into the oil. A new model is needed to properly capture the physics of solvent mass transfer in these viscous oil systems, which allows for diffusion becoming zero as solvent content also approaches zero. This observed solvent penetration shape is only seen in these highly viscous oil systems. The results of this study indicate that diffusion coefficients are not only a function of concentration, but also of oil viscosity and this is missing from current models of solvent diffusivity within oil.

Acknowledgements

The authors wish to express gratitude to the the Asphaltene and Emulsion Research Group (Professor Harvey Yarranton) for collaboration and advice in this project, and for providing samples of cleaned Peace River bitumen for testing. Grosmont bitumen was provided by Laricina Energy Ltd. Financial support for this work has come partially from the NSERC Chair in Fundamentals of Unconventional Resources (FUR), the University of Calgary, and its industrial sponsors: Laricina Energy, Husky Energy, Athabasca Oil Corp, Maersk Oil, Suncor, Brion Energy, CNRL, Devon, Foundation CMG and Alberta Innovates.

NOMENCLATURE

Letter Symbol	Quantity	Dimensions
English		
C	Concentration	(m ³ /m ³)
C_0	Maximum concentration of solvent vapour at the saturated oil-solvent interface	(m ³ /m ³)
C3	Propane	
C5	Pentane	
D	Diffusion coefficient	(cm ² /s)
DME	Di-methyl ether	
P	System pressure	(kPaa)
P_{sat}	Saturation (dew point) pressure of solvent at test temperature	(kPaa)
\times	Distance away from original solvent-oil interface	cm
Symbols		
ρ_{meas}	Density of oil-solvent mixture	(g/cm ³)
ρ_o	Denisty of oil (bitumen)	(g/cm ³)
ρ_s	Density of solvent	(g/cm ³)

References

- Ahmadloo, F. and Yang, P., "Solvent-Assisted Start-up of SAGD Wells in Long Lake Project", SPE 170052, SPE Heavy Oil Conference, Calgary, AB CANADA, Jun 10–12, 2014.

- Badamchi-Zadeh, A., Yarranton, H., and Maini, B., "Phase Behavior and Physical Property Measurement for Vapex Solvents: Propane, Carbon Dioxide and Athabasca Bitumen", SPE 165505, SPE Heavy Oil Conference, Calgary, AB CANADA, Jun 11–13, 2013.
- Etmnan, S.R., Maini, B.B., Chen, Z., and Hassanzadeh, H., "Constant-Pressure Technique for Gas Diffusivity and Solubility Measurements in Heavy Oil and Bitumen", *Energy & Fuels*, **24** (1), 533–549, 2010.
- Ghaderi, S.M., Tabatabaie, S.M., Hassanzadeh, H. and Pooladi-Darvish, M., "Estimation of concentration-dependent diffusion coefficient in pressure-decay experiment of heavy oils and bitumen", *Fluid Phase Equilibria*, **305**, 132–144, 2011.
- Guerrero-Aconcha, U. and Kantzas, A., "Diffusion of Hydrocarbon Gases in Heavy Oil and Bitumen", SPE 122783, 2009 SPE Latin American and Caribbean Petroleum Engineering Conference, Cartagena, Colombia, May 31–Jun 3, 2009.
- Guerrero-Aconcha, U., Salama, D. and Kantzas, A., "Diffusion Coefficient of n-alkanes in Heavy Oil", SPE 115346, 2008 SPE Annual Technical Conference and Exhibition, Denver, CO USA, Sept 21–24, 2008.
- Haghighat, P. and Maini, B., "Effect of Temperature on VAPEX Performance", *SPE 157799, J. Can. Pet. Tech.*, **52** (6), 408–416, Nov 2013.
- International DME Association (IDA)* website: <http://www.aboutme.org/index.asp?bid=234#Q1.1>, Dec 2014.
- Ivory, J., Chang, J., Coates, R. and Forschner, K., "Investigation of Cyclic Solvent Injection Process for Heavy Oil Recovery", *J. Can. Pet. Tech.*, **49** (9), 22–33, Sept 2010.
- Jiang, T., Jia, X., Zeng, F. and Gu, Y., "A Novel Solvent Injection Technique for Enhanced Heavy Oil Recovery: Cyclic Production with Continuous Solvent Injection", SPE 165455, SPE Heavy Oil Conference, Calgary, AB CANADA, Jun 11–13, 2013.
- Kristoff, B.J., Knorr, K.D., Preston, C.K., Worth, K., and Sawatzky, R., "Joint Implementation of Vapour Extraction Heavy Oil Recovery Process", 2008-468, World Heavy Oil Congress, Edmonton, AB CANADA, Mar 10–12, 2008.
- Li, W. and Mamora, D.D., "Simulation Investigation of Solvent Co-Injection in Vapor and Liquid Phase to Reduce Shale Barrier Impact on SAGD Performance", SPE 133298, SPE Western North America Regional Meeting, Anaheim, CA USA, May 26–30, 2010.
- Luo, H., and Kantzas, A., "Investigation of Diffusion Coefficients of Heavy Oil and Hydrocarbon Solvent Systems in Porous Media", SPE 113995, Improved Oil Recovery Symposium, Tulsa, OK USA, Apr 19–23, 2008.
- Memon, A.I., Gao, J., Taylor, S.D., Davies, T.L. and Jia, N., "A Systematic Workflow Process for Heavy Oil Characterization: Experimental Techniques and Challenges", SPE 137006, Unconventional Resources and International Petroleum Conference, Calgary, AB CANADA, Oct 19–21, 2010.
- Nenniger, J.E. and Dunn, S.G., "How Fast is Solvent Based Gravity Drainage?", PS-2008-139, 59th Annual Technical Meeting of the Petroleum Society, Calgary, AB CANADA, Jun 17–19, 2008.
- Rassenfoss, S., "Oil Sands Get Wired–Seeking More Oil, Fewer Emissions", *SPE 0912-0034, J. Pet. Tech.*, **64** (3), 34–45, Sept 2012.
- Salama, D., Kantzas, A., "Monitoring of Diffusion of Heavy Oils with Hydrocarbon Solvents in the presence of Sand", SPE 97855, International Thermal Operations and Heavy Oil Symposium, Calgary, AB CANADA, Nov 1–3, 2005.
- Sarafianos, N., "An analytical method of calculating variable diffusion coefficients", *J. Mat. Sc.*, **21**, 2283–2288, 1986.

- Sheikha, H., Pooladi-Darvish, M., and Mehrotra, A.K., “Development of graphical methods for estimating the diffusivity coefficient of gases in bitumen from pressure-decay data”, *Energy & Fuels*, **19** (5), 2041–2049, 2005.
- Song, L., Kantzas, A., and Bryan, J., “Experimental Measurement of Diffusion Coefficient of CO₂ in Heavy Oil Using X-Ray Computed-Assisted Tomography under Reservoir Conditions”, SPE 137545, 2010 Canadian Unconventional Resources and International Petroleum Conference, Calgary, AB CANADA, Oct 19–21, 2010.
- Taupy, J-A., “DME a Clean Fuel for the Future”, SPE IPTC 11754, SPE International Technology Conference, Dubai, UAE, Dec 4–6, 2007.
- Tharanivasan, A.K., Yang, C., and Gu, Y., “Comparison of three different interface mass transfer models used in experimental measurement of solvent diffusivity in heavy oil”, *J. Pet. Science & Engg*, **44** (3-4), 269–282, 2004.
- Upreti, S.R. and Mehrotra, A.K., “Experimental measurement of gas diffusivity in bitumen: results for carbon dioxide”, *Ind. & Engg. Chemistry Research*, **39** (4), 1080–1087, 2000.
- Wen, Y., Kantzas, A., Wang, G. J., “Estimation of diffusion coefficients in bitumen solvent mixtures using X-ray CAT scanning and low field NMR”, PS2004-064, 53rd Annual Technical Meeting of the Petroleum Society, Calgary, AB CANADA, Jun 8–10, 2004.
- Yang, C. and Gu, Y., “A new experimental method for measuring gas diffusivity in heavy oil by the dynamic pendant drop volume analysis (DPDVA)”, *Ind. Eng. Chem. Res.*, **44**, 4474–4483, 2005.
- Zhang, Y., Hyndman, C.L. and Maini, B., “Measurement of Gas Diffusivity in Heavy Oils”, PS-98-63, 49th Annual Technical Meeting of the Petroleum Society, Calgary, AB CANADA, Jun 8–10, 1998.