# Efficient Displacement of Heavy Oil by Use of Three Hydrocarbon Phases

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# Summary

Mixtures of oil with solvent gas can exhibit three-hydrocarbonphase behavior at reservoir conditions, where the solvent-rich liquid  $(L_2)$  phase coexists with the gaseous (V) and oleic  $(L_1)$  phases. Three-hydrocarbon-phase behavior has been studied in the literature for carbon dioxide  $(CO<sub>2</sub>)$  floods and enriched-gas floods at relatively low temperatures. Prior research on heavy-oil displacement with enriched gas presented that displacement efficiency at a given throughput can be nonmonotonic with respect to gas enrichment. Slimtube experiments for such displacements showed that oil recovery increased first, then decreased, and increased again with increasing gas enrichment. An optimum displacement with a high efficiency of more than 90% was observed when threehydrocarbon-phase flow was present. However, detailed mechanisms for such an optimum displacement with three phases have not been explained in the literature.

In this research, we investigate mass transfer on multiphase transitions between two and three phases for three-hydrocarbonphase displacements. Simple conditions are derived for the multiphase transitions that yield high local displacement efficiency by three hydrocarbon phases. The derivation is based on the generalized mass conservation for a multiphase transition in 1D gas injection. The conditions derived are applied to explain nonmonotonic oil recovery in quaternary displacements and the West Sak oil displacements.

Oil recovery at a given throughput can be nonmonotonic with respect to pressure or gas enrichment. Such a nonmonotonic trend can occur when local oil displacement by three hydrocarbon phases becomes more efficient, but slower, with decreasing pressure or decreasing gas enrichment. An optimum pressure or enrichment can occur as a consequence of the balance between the local displacement efficiency and the propagation rate of three hydrocarbon phases. The West Sak oil displacement with enriched gas studied in this research yields a high displacement efficiency of more than 90% at 1.5 hydrocarbon pore volumes (PV) injected at 53% methane  $(C_1)$  dilution.

#### Introduction

Solvent injection is a widely used method for enhanced oil recovery (EOR) (Lake 1989; Taber et al. 1997; Orr 2007). Its implementation has been made for a wide variety of oil reservoirs: in West Texas (Mizenko 1992; Stein et al. 1992; Tanner et al. 1992), in Alaska (McGuire et al. 2001), in Canada (Malik and Islam 2000), and in the North Sea (Varotsis et al. 1986). Coinjection of steam and solvent could further widen the applicability of solvent to extraheavy oil and bitumen reservoirs. A few pilot tests for the coinjection were reported in the literature (Gupta et al. 2005; Gupta and Gittins 2006; Dickson et al. 2011).

Reliable design of solvent injection requires detailed understanding of oil-displacement mechanisms. Displacement theory for solvent injection has been established for conventional twohydrocarbon phases (Orr 2007). Multicontact miscibility (MCM) between two phases can be developed through vaporizing, condensing, or combined condensing/vaporizing mechanisms (Dindoruk 1992; Johns 1992). An important design parameter for solvent injection is the thermodynamic minimum miscibility pressure (MMP). The thermodynamic MMP is the minimum displacement pressure at which complete miscibility is developed along a composition path from the injection-gas composition to the reservoir-oil composition for 1D flow in the absence of dispersion. Efficient methods have been developed for MMP calculation, where phase behavior and flow are effectively decoupled (Johns and Orr 1996; Ahmadi and Johns 2011).

Solvent injection is often conducted at partially miscible (PM) (or immiscible) conditions because it can be costly and difficult to achieve MCM conditions in situ, especially in a heavy-oil reservoir. Also, many solvent/oil mixtures can exhibit three hydrocarbon phases with partial miscibility at reservoir conditions (Gardner et al. 1981; Khan et al. 1992; Creek and Sheffield 1993). These are the oleic  $(L_1)$ , solvent-rich liquid  $(L_2)$ , and gaseous (V) phases. The three-hydrocarbon-phase behavior is characteristic of highly sizeasymmetric mixtures as observed for *n*-alkane binaries and  $CO<sub>2</sub>-n$ alkane binaries (Rowlinson 1959; Polishuk et al. 2004). As summarized by Peters (1994), three-phase behavior bounded by two critical endpoints (CEPs) has been observed for n-alkane binaries;  $C_1/nC_6$ ,  $C_1/nC_7$ ,  $C_2/n$ -alkanes from  $nC_{18}$  through  $nC_{25}$ ; and  $C_3/n$ alkanes heavier than  $nC_{30}$ . A CEP is a critical state where two of the three equilibrium phases become critical (Uzunov 1993). There are two types of CEPs: lower CEP (LCEP), where the  $L_1$  and  $L_2$ phases merge in the presence of the V phase  $(L_1 = L_2 - V)$ , and upper CEP (UCEP), where the V and  $L_2$  phases merge in the presence of the  $L_1$  phase  $(L_1 - L_2 = V)$ . In the abbreviated symbolic notation, the critical and noncritical equilibrium states are expressed by use of "=" and "-", respectively.

Modeling of the complex three-phase behavior has been also conducted by use of various equations of state (EOSs): the van der Waals EOS (van Konynenburg 1968; Scott and van Konynenburg 1970; van Konynenburg and Scott 1980; Bluma and Deiters 1999), the Redlich-Kwong EOS (Deiters and Schneider 1976; Deiters and Pegg 1989), the Peng-Robinson EOS (Gauter 1999; Gauter et al. 1999; Mushrif 2004; Yang 2006; Mushrif and Phoenix 2008), and the Soave-Redlich-Kwong EOS (Gregorowicz and de Loos 1996). The results show that a cubic EOS is capable of predicting three-phase behavior (van Konynenburg 1968).

There are major heavy-oil reservoirs on the North Slope of Alaska, such as the West Sak, Schrader Bluff, and Kuparuk oil reservoirs. The primary recovery and waterflooding were relatively inefficient in these heavy-oil reservoirs mainly because of high oil viscosity. Solvent injection has been studied because Prudhoe Bay artificial-lift gas and Prudhoe Bay natural-gas liquid are both available as solvent (Sharma et al. 1989; Hornbrook et al. 1991; DeRuiter et al. 1994; Godbole et al. 1995; Khataniar et al. 1999; McKean et al. 1999; Wang and Strycker 2000; Madarapu et al. 2002; Li et al. 2003; Wang et al. 2003; McGuire et al. 2005; Targac et al. 2005; Aghbash and Ahmadi 2012). Conventional thermal methods were considered to be impractical because of high well costs, large well spacing, and thick permafrost (McGuire et al. 2005).

Mixtures of heavy oil and solvent exhibit complex multiphase behavior at low reservoir temperature (50-100°F) because of proximity to the permafrost in the region (DeRuiter et al. 1994). A number of authors presented experimental phase-behavior studies for these heavy oils: the West Sak oil (Shu and Hartman 1988; Roper 1989; Sharma et al. 1989; Hornbrook et al. 1991; Okuyiga 1992; DeRuiter et al. 1994; Mohanty et al. 1995; McGuire et al.

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This paper (SPE 165470) was accepted for presentation at the SPE Heavy Oil Conference Canada, Calgary, 11–13 June 2013, and revised for publication. Original manuscript received for review 29 March 2013. Revised manuscript received for review 6 December 2013. Paper peer approved 17 January 2014.

2005), the Schrader Bluff oil (Inaganti 1994; Reid 1994; Khataniar et al. 1999; McKean et al. 1999; Wang and Strycker 2000; Madarapu et al. 2002), and the Kuparuk oil (Godbole et al. 1995). Multiphase behavior involving the  $L_1$ ,  $L_2$ , and V phases was observed in their static experiments and slimtube tests.

Various numerical-simulation studies were also conducted with concerns about sweep efficiency, which is typically low for gas injection in a viscous oil reservoir because of gravity segregation; front instability; and heterogeneity (Mohanty et al. 1995; Guler et al. 2001; Madarapu et al. 2002; Li et al. 2003; Wang et al. 2003; Sohrabi et al. 2007). Most of the studies considered water-alternating-gas (WAG) injection. In numerical simulations by Guler et al. (2001) and Wang et al. (2003), oil displacement by the  $L_2$  phase exhibited less gravity segregation than expected from conventional oil displacement by gas. This was because the liquid-like density of the  $L_2$  phase at the reservoir conditions made the density difference between the  $L_1$  and  $L_2$  phases less significant. Also, the formation of multiple liquid phases during the displacements was found to make displacement fronts less unstable (Mohanty et al. 1995; Sohrabi et al. 2007). This was consistent with experimental observations by DeRuiter et al. (1994) and Khataniar et al. (1999).

The in-situ formation of multiple liquid phases was observed to decrease the total mobility of the transition zone in gas displacements (Henry and Metcalfe 1983). The reduced injectivity observed in the North Cross Devonian  $CO<sub>2</sub>$  flood was partially attributed to the formation of three hydrocarbon phases (Pontious and Tham 1978). Patel et al. (1987) concluded that phase behavior does not necessarily create injectivity decreases by itself. Rogers and Grigg (2001) stated that there is no clear experimental evidence that multiphase behavior effects result in field-observed fluid mobilities. Targac et al. (2005) described that the injectivity in West Sak has been substantially increased with the evolution in horizontal and multilateral drilling technology. Guler et al. (2001) stated that the presence of initial mobile water in the Schrader Bluff oil reservoir could increase the solvent injectivity. An extensive literature analysis on injectivity behavior in various  $CO<sub>2</sub>$ floods can be found in Rogers and Grigg (2001).

A large three-hydrocarbon-phase region was observed during slimtube experiments in DeRuiter et al. (1994) and Mohanty et al. (1995). Mohanty et al. (1995) also confirmed three-hydrocarbonphase flow in 1D numerical simulations by use of the UTCOMP simulator (Chang et al. 1990). The UTCOMP simulator is an EOS compositional multiphase reservoir simulator developed at the University of Texas at Austin. It is based on the implicit-pressure/ explicit-concentration (IMPEC) formulation. However, coexistence of the three hydrocarbon phases was much less obvious in multidimensional simulations of solvent injection for Alaskan heavy oils in Guler et al. (2001) and Madarapu et al. (2002). These results indicate that gravity, channeling, and dispersion affect compositional propagation in the multidimensional multiphase flow.

Chang et al. (1994) and Chang (1990) presented a systematic investigation of reservoir-flow patterns in  $CO<sub>2</sub>$  floods, such as viscous fingering, channeling, gravity override, and dispersive flow. Multidimensional numerical simulations of  $CO<sub>2</sub>$  floods were conducted by use of the UTCOMP simulator with a wide range of endpoint mobility ratio, gravity number, effective aspect ratio, longitudinal- and transverse-Péclet number, correlation length, and Dykstra-Parsons coefficient. They showed that viscous fingering was unlikely as a dominant-flow pattern for field-scale  $CO<sub>2</sub>$  flooding under secondary conditions without use of WAG injection, which would reduce the tendency of fingering. They concluded that fingering should be taken into account under typical laboratory conditions of low effective aspect ratio and low permeability variation, but fingering would be much less likely to be important under reservoir conditions of high effective aspect ratio. The dominant flow patterns were channeling, gravity override, and dispersive flow for most of the cases studied. The fluid model used was a ternary model of a Maljamar separator oil given by Ogino (1988). Three hydrocarbon phases were not predicted with this ternary fluid, as presented in Chang (1990). The investigation by Tchelepi and Orr (1994) also suggested that channeling and gravity override would be dominant

Heavy-oil displacement by three hydrocarbon phases is difficult to interpret even for 1D flow with no gravity (DeRuiter et al. 1994), which is the main focus of this paper. Prior studies showed that 1D oil displacement with three hydrocarbon phases can exhibit displacement efficiency that is nonmonotonic with respect to gas enrichment at a given throughput. DeRuiter et al. (1994) and Mohanty et al. (1995) conducted slimtube experiments for the West Sak oil with enriched gas. Their results showed that oil recovery at 1.2 PV injected (PVI) first decreased, then increased, and finally decreased again with decreasing gas enrichment. Oil recoveries at 1.2 PVI were 97, 87, 89, 93 and 65% at 32-, 42-, 51- , 62-, and 70%-C<sub>1</sub> dilution, respectively. A maximum of 93% at 62%-C<sub>1</sub> dilution was substantially higher than 87% at a lower C<sub>1</sub> dilution of 42%.

DeRuiter et al. (1994) speculated that the nonmonotonic trend was associated with the coexistence of three hydrocarbon phases and their effects on the front mobility. The improvement in mobility ratio can improve sweep efficiency in multidimensional floods (Mohanty et al. 1995). However, the effect of miscibility (i.e., compositional phase behavior) would dominate over the fractional-flow effect in terms of local displacement efficiency in this PM flow with significant mass transfer among phases. Mohanty et al. (1995) later explained that oil recovery at 1.2 PVI was higher at 62%-C<sub>1</sub> dilution than at 51%-C<sub>1</sub> dilution because the  $L_2$ phase was nearly miscible with the  $L_1$  phase at the three-phase displacement front; oil became less viscous at the front; and the front moved fast enough to exit the slimtube by 1.2 PVI. No detailed theoretical explanation has been given in the literature as to what causes gas enrichment to decrease oil recovery.

The existing theory of gas injection does not explain a nonmonotonic trend of PM displacement efficiency. The length of the shortest tie-line monotonically decreases as pressure or gas enrichment increases in the conventional two-phase displacement when the fluid is properly characterized (Ahmadi 2011). Thus, the efficiency of the conventional two-phase displacement tends to increase monotonically until MCM is approached. A question then arises as to why the efficiency of three-hydrocarbon-phase displacement can decrease as gas enrichment (or displacement pressure) increases. We present in this paper that the reason is associated with multiphase transitions between two and three phases in threephase PM displacements. The main novelty of this research is that simple conditions are developed for the mass transfer on multiphase transitions that yield high local displacement efficiency by three PM phases. Because of the complex phase behavior, the focus of this paper is on 1D oil displacement with no gravity. Decoupling of local-oil displacement from the effects of reservoir-flow patterns enables us to analyze detailed mass-transfer mechanisms during the complex multiphase displacements.

In the subsequent sections, we first discuss multiphase behavior in solvent injection by use of a synthetic quaternary system, which exhibits a decreasing trend of oil recovery with increasing displacement pressure or solvent enrichment. We then present a theoretical analysis of phase transitions in three-hydrocarbonphase displacement. Conditions are derived for efficient oil displacement by three hydrocarbon phases, and are explained in detail by use of simulation cases with the quaternary system. Finally, the efficiency conditions are confirmed in fine-scale simulations for enriched-gas injection for the West Sak oil.

# Characteristics of Oil Displacement With Three Hydrocarbon Phases

This section describes general characteristics of three-hydrocarbon-phase displacement in terms of multiphase transitions and their effects on displacement efficiency. The main difference



Fig. 1—Schematics of phase behavior in two- and three-phase displacements. The oleic phase is given as  $L_1$ . A nonoleic phase  $(N_1)$  appears at the displacement front for two- and threephase displacements. For a three-phase displacement, another nonoleic phase  $(N_2)$  appears at the leading edge of the threephase region. One of the two nonoleic phases  $(N_1 \text{ and } N_2)$  in the three-phase region disappears at the trailing edge of the three-phase region. The nonoleic phase  $(N_3)$  in the upstream two-phase region is either  $N_1$  or  $N_2$ , depending on the phase behavior involved there. Four possible patterns for three-phase displacement are also presented.

between two- and three-phase displacements is that the latter involves multiphase transitions between two and three phases. Fig. 1 schematically shows phase behavior during two- and threephase displacements. A two-phase displacement involves the  $L_1$ phase and a nonoleic  $(N_1)$  phase. Although the  $N_1$  phase is often the V phase in typical gasfloods, we do not specify its phase identity in the schematic, for generality. A phase transition between one and two phases occurs at the displacement front, where the  $N_1$ phase appears. Complete evaporation of the  $L_1$  phase is invisible in the schematic because the evaporation wave is normally much slower than the displacement front, especially in the presence of dispersion.

Phase behavior for three-phase displacement of oil is more involved. Two nonoleic phases appear in sequence in the direction from the producer to the injector. The nonoleic phase that appears first at the displacement front is referred to as  $N_1$ . The  $N_2$  phase then appears at the leading edge of the three-phase region, which is at equilibrium with the  $L_1$  and  $N_1$  phases in the three-phase region. One of the two nonoleic phases disappears at the trailing edge of the three-phase region. The nonoleic phase that coexists with the  $L_1$  phase in the upstream two-phase region is referred to as  $N_3$ , which is either  $N_1$  or  $N_2$  depending on the phase transition there.

There are four patterns for phase transitions for the three-phase displacement in Fig. 1 because the  $N_1/N_3$  pair can be either  $V/V$ , or  $V/L_2$ , or  $L_2/V$ , or  $L_2/L_2$ . That is, the four patterns for  $(N_1, N_2,$  $N_3$ ) are as follows:  $(V, L_2, V)$ ,  $(V, L_2, L_2)$ ,  $(L_2, V, V)$ , and  $(L_2, V, V)$  $L<sub>2</sub>$ ). The two phases at the displacement front are typically the V and  $L_1$  phases because of a fast-traveling  $C_1$  bank. For the two phases upstream of the three-phase region, however, both  $L_1/V$ and  $L_1/L_2$  are common depending on phase behavior near the injection-gas composition at the operating temperature and pressure. Although it is possible to have a direct transition between one phase and three phases without involving two-phase equilibrium, as shown in LaForce and Johns (2005a), we do not consider this type of phase transition in this research.

Existence of three phases during oil displacement with solvent indicates that the composition path goes through part of a threephase region in composition space at the temperature and pressure. The entire three-phase region is not necessarily realized

along the composition path. Thus, the three-phase behavior encountered during the displacement is considered as part of the entire three-phase region. The entire three-phase region can be considered to be bounded by two CEP behaviors in composition space (Okuno 2009; Okuno et al. 2011), as illustrated in Appendix A. A CEP is a critical phase behavior in which two of the three phases merge in the presence of the other immiscible phase. The  $L_1$  and  $L_2$  phases merge in the presence of the V phase at the LCEP, whereas the  $L_2$  and  $V$  phases merge in the presence of the  $L_1$  phase at the UCEP. Three-phase behavior bounded by the two types of CEPs is well-documented in the literature especially for n-alkane binaries (Rowlinson and Freeman 1961; Kohn et al. 1966) and  $CO_2/n$ -alkane binaries (Enick et al. 1985; Galindo and Blas 2002). Note that there are two equilibrium phases at a CEP; i.e., it is a tie-line rather than a point in composition space. In this paper, a CEP is sometimes called a CEP tie-line to avoid potential confusion.

Okuno et al. (2011) studied mechanisms of three-phase displacement of conventional oil with CO<sub>2</sub> solvent. Most of the phase transitions in their study were as follows:  $V$  for  $N_1$ ,  $L_2$  for  $N_2$ , and V for  $N_3$ . They used four components to conduct a systematic investigation of oil-displacement mechanisms involving three phases bounded by the UCEP and LCEP tie-lines. Results showed that high displacement efficiency of more than 90% at 2.0 hydrocarbon PVI (HCPVI) could be achieved when the composition path traversed near the UCEP and LCEP tie-lines. Oil components were efficiently extracted by the  $L_2$  phase because of near-LCEP behavior at the leading edge of three phases. Near-UCEP behavior at the trailing edge of three phases then allowed the  $L_2$  phase to efficiently merge into the  $V$  phase. That is, the  $L_2$  phase served as a buffer between the immiscible  $V$  and  $L_1$  phases within the threephase region. They also confirmed this displacement mechanism for multicomponent systems based on west Texas oils. Although nearly piston-like displacements were simulated with three phases bounded by the CEP tie-lines, it was uncertain whether MCM could be developed through the CEP behavior.

Recent research on analytical solutions for three-phase displacements has significantly improved our understanding of miscibility development in three-phase flow (LaForce and Johns 2005b; LaForce et al. 2008a, 2008b; LaForce and Orr 2008, 2009; LaForce 2012). These studies considered analytical composition paths and miscibility development in water and gas injection by use of three and four components on the basis of the method of characteristics (MOC). The four components consisted of water,  $CO<sub>2</sub>$ , and two hydrocarbon components. The quaternary cases with miscible-gas/water injection presented a CEP in composition space, at which the two hydrocarbon phases were critical in the presence of the aqueous (W) phase (i.e., a CEP of type  $L_1 = V -$ W). This was the only CEP in composition space in their research because the W phase was immiscible with the hydrocarbon phases. Their results indicated that MCM could be developed not only at the two-phase critical point  $(L_1 = V)$ , but also on the CEP tie-line  $(L_1 = V - W)$ . In such a case, the initial oil in the L/W region was completely displaced by  $CO<sub>2</sub>$  in the V/W region through the CEP tie-line. For complex three-hydrocarbon-phase flow with critical endpoints, however, analytical solutions by use of the MOC have not been presented in the literature, to the best of our knowledge.

# Nonmonotonic Oil Recovery by Use of a Quaternary System

This section describes nonmonotonic oil recovery by use of a quaternary fluid, which is modeled after the Schrader Bluff oil model in Guler et al. (2001). Fine-scale compositional simulations are performed for linear oil displacement with no gravity. The UTCOMP simulator (Chang et al. 1990) with the Peng-Robinson EOS (Peng and Robinson 1976) is used for all flow simulations in this research. The UTCOMP simulator has been used in various papers on gas-injection theory (Mohanty et al. 1995; Johns et al. 2000, 2004; Solano et al. 2001). Because of numerical dispersion, the numerical-simulation results deviate from the analytical





solutions based on the MOC for 1D gas injection. The deviation diminishes as the Péclet number becomes higher with more gridblocks. Recently, van Odyck et al. (2012) and Mallison et al. (2005) developed methods for accurately simulating displacement processes.

The four components consist of one light pseudocomponent (PC1), one intermediate pseudocomponent (PC2), and two heavy pseudocomponents (PC3 and PC4). Their properties are given in Tables 1 and 2. The oil gravity is calculated to be approximately 10° API. The injection gas consists of 20% PC1 and 80% PC2.

Fig. 2 shows the pressure/temperature (P/T) diagrams calculated for the quaternary oil and injection gas by use of PVTsim software (Calsep 2012). The bubblepoint pressure at the reservoir temperature of 86°F is 1,953 psia for the oil. The bubble- and dewpoint pressures at 86°F are 658 psia and 334 psia, respectively, for the injection gas. The critical point of the injection gas is calculated to be 144.88°F and 836.38 psia. Fig. 3 presents calculated densities and viscosities for the injection gas at different pressures at 86°F. The injection-gas density rapidly increases with pressure within the two-phase region, and becomes more than 25  $lbm/ft<sup>3</sup>$  above the bubblepoint of 658 psia. The injection-gas viscosity calculated by use of the Lohrenz-Bray-Clark model (Lohrenz et al. 1964) increases monotonically with pressure.



Fig. 3—Viscosities and densities for the injection gas calculated at 86<sup>º</sup> F. Viscosity calculation is modeled after the Lohrenz-Bray-Clark model (Lohrenz et al. 1964). The injection-gas properties are given in Tables 1 and 2. Two phases are present at pressures between 334 and 658 psia.



Fig. 2—P/T diagrams of the quaternary oil and injected gas given in Tables 1 and 2. The solid line is the two-phase boundary for the initial oil composition and the dashed line is the three-phase region. The dotted line is the two-phase boundary for the injection gas. The Peng-Robinson EOS is used. The bubblepoint pressure for the oil is 1,953 psia at the reservoir temperature of 86<sup>º</sup> F. The dewpoint and bubblepoint pressures for the injected gas at 86<sup>º</sup> F are 334 and 658 psia, respectively.

Fig. 4 gives the pressure/solvent-mole-fraction diagram calculated for mixtures of the oil and the injection gas at 86°F by use of the PVTsim software. Two immiscible liquid phases are present at a wide range of solvent concentrations. Three phases exist between the  $L_1/L_2$  region and the  $L_1/V$  region. Mixing of a small amount of the oil with the injection gas causes three-phase behavior at pressures between 211 and 658 psia. Similar phase behavior was presented for Alaskan North Slope heavy oils and solvents in Okuyiga (1992), Godbole et al. (1995), Khataniar et al. (1999),



Fig. 4—Pressure/solvent-mole-fraction diagram at 86<sup>º</sup> F for mixtures of the quaternary oil and the injection gas given in Tables 1 and 2. The oleic, solvent-rich-liquid, and gaseous phases are given as  $L_1$ ,  $L_2$ , and V, respectively.



 $PC4 \longleftarrow$  PC1  $L_1-V$  $L_1$ - $L_2$ PC2 Injection gas Projection of composition path 3-phase region  $L_1$ 

Fig. 5—PC3-free ternary subsystem for the quaternary displacement at 700 psia at 86<sup>º</sup> F. The bold solid lines are phase boundaries. The solid lines are tie-lines. The dashed line is the projection of the composition at 0.33 HCPVI on this ternary plane. The oil and gas properties are given in Tables 1 and 2.

Fig. 6—PC3-free ternary subsystem for the quaternary displacement at 1,000 psia at 86<sup>º</sup> F. The bold solid lines are phase boundaries. The solid lines are tie-lines. The dashed line is the projection of the composition at 0.33 HCPVI on this ternary plane. The oil and gas properties are given in Tables 1 and 2.

TABLE 3-RESERVOIR PROPERTIES FOR SIMULATIONS OF 1D OIL DISPLACEMENTS						
			Corey Model			
<b>Dimensions</b>	$10\times1\times10$ ft <sup>3</sup>	<b>Relative Permeability</b>	W	$L_1$	V	L <sub>2</sub>
Number of cells	$1\times1.000\times1$	<b>Residual Saturation</b>	0.4	0.2	0.05	0.05
Porosity	0.2	<b>Endpoint Relative Permeability</b>	0.35	0.5	0.65	0.65
Permeability	1.000 md	Exponent	3	3	3	3
		<b>Initial Saturation</b>	0.4	0.6	$\Omega$	0

McKean et al. (1999), Guler et al. (2001), and Wang et al. (2003). The three-phase behavior in the vicinity of the solvent composition can be seen in ternary subsystems. Figs. 5 and 6 present phase behavior on the PC3-free ternary subsystems at 700 and



Fig. 7—Oil recovery simulated for the quaternary displacements at different pressures at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2. A maximum of 78.69% is observed for recovery at 2.0 HCPVI at 800 psia. At 2.0 HCPVI, the threephase displacement at 800 psia is 19% more efficient than the two-phase displacement at 2,500 psia. The trailing edge of the three-phase region reaches the outlet at 1.1273 HCPVI at 700 psia, 0.9458 HCPVI at 800 psia, 0.8852 HCPVI at 1,000 psia, 0.7338 HCPVI at 1,500 psia, and 0.6413 HCPVI at 1,750 psia. Oil recovery at breakthrough of the three-phase trailing edge is 78.42% at 700 psia, 78.37% at 800 psia, 78.30% at 1,000 psia, 68.86% at 1,500 psia, and 59.21% at 1,750 psia. Oil displacement by three phases is faster, but less efficient, with increasing pressure.

1,000 psia, respectively, at 86°F. The gas composition is near the three-phase region at 700 psia, but not at 1,000 psia.

Table 3 shows the reservoir properties used in simulations in this research. The relative permeability is based on the Corey model. The number of gridblocks is 1,000, with a uniform gridblock size of 1 ft in the displacement direction. The initial water saturation is at the residual saturation of 0.4, and water does not flow in all simulations in this study. Gas injection is continued until the trailing edge of the three-hydrocarbon-phase region reaches the outlet when three phases are present. The quaternary oil displacements are performed at different pressures: 500, 600, 700, 800, 1,000, 1,500, 1,750, and 2,500 psia.

Fig. 7 presents that the displacement efficiencies at 2.0 HCPVI are 71.76, 72.18, 78.42, 78.69, 78.39, 69.59, 62.30, and 59.27% at 500, 600, 700, 800, 1,000, 1,500, 1,750, and 2,500 psia, respectively. A maximum of 78.69% is observed at 800 psia, and the oil recovery at 2.0 HCPVI becomes substantially lower at higher pressures. Three phases are present for the displacements at pressures from 500 to 1,750 psia, but not at 2,500 psia. The 1D oil recovery at 800 psia is 19% more efficient than that at 2,500 psia at 2.0 HCPVI.

Local displacement efficiency at PM conditions depends on the level of miscibility, which affects propagation rates of components. Phase behavior during the displacement is then determined by the resulting compositional variation at the operating pressure and temperature. Fig. 7 also shows oil recovery at breakthrough of the trailing edge of the three-phase region to see the local displacement efficiency by three phases. The trailing edge of the three-phase region reaches the producer at 1.13 HCPVI at 700 psia, 0.95 HCPVI at 800 psia, 0.89 HCPVI at 1,000 psia, 0.73 HCPVI at 1,500 psia, and 0.64 HCPVI at 1,750 psia. Because the trailing edge of the three-phase region is extremely slow at 500 and 600 psia, it is not shown for these pressures. Fig. 7 indicates that the local displacement by three phases becomes less efficient, but propagation of three phases becomes faster with increasing pressure between 700 and 1,750 psia. For example, even though propagation of three phases is faster at 1,750 psia than at 800 psia,



Fig. 8—Phase behavior along the composition path in the quaternary displacement at 700 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2. A few tie-lines are shown in the upstream two-phase region and in the downstream two-phase region. A few tie triangles are shown in the three-phase region to show a continuous variation between the leading and trailing edges of the three-phase region.

the local displacement by three phases is less efficient at 1,750 psia than at 800 psia. As a result, the displacement efficiency at a fixed throughput of 2.0 HCPVI is 16% higher at 800 psia than at 1,750 psia, as shown in Fig. 7.

Fig. 8 presents the composition path and phase behavior in the displacement at 700 psia. The phase behavior pattern is observed as follows: V for  $N_1$ ,  $L_2$  for  $N_2$ , and  $L_2$  for  $N_3$ . This is also true in the other three-phase displacements presented in later sections. Because the pressure is below the bubblepoint (1,953 psia at  $86^{\circ}$ F), the initial oil is in the  $V/L_1$  region. The initial high mobility V phase results in formation of an oil bank, as can be seen along the initial oil tie-line [see LaForce and Johns (2010) for detailed explanation of the effect of the initial V-phase saturation on oil recovery]. The tie triangle at the leading edge of the three-phase region is elongated, and the  $L_1$  and  $L_2$  phases are close to each other. The distance between the  $L_1$  and  $L_2$  compositions is 0.0547 at the leading edge. The tie triangle changes its size and shape in the three-phase region, as shown by a few shaded tie triangles in Fig. 8. The tie triangle at the trailing edge of the three-phase region shows that the coexisting phases are highly immiscible with each other. On this tie triangle, the distance is 0.6875 for  $\|\underline{x}_{L_1} - \underline{x}_V\|_2$ , 0.3956 for  $\|\underline{x}_{L_2} - \underline{x}_V\|_2$ , and 0.6835 for  $\|\underline{x}_{L_1} - \underline{x}_V\|_2$ , 0.3956 for  $\|\underline{x}_{L_2} - \underline{x}_V\|_2$ , and 0.6835 for  $\|\underline{x}_{L_1} - \underline{x}_{L_2}\|_2$ , where  $\underline{x}_j$  is the composition of equilibrium phase *j*.  $-\underline{x}_{L_2} \|_2$ , where  $\underline{x}_j$  is the composition of equilibrium phase j.



Fig. 10—Simulated phase mole fractions at 0.33 HCPVI for the quaternary displacement at 700 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 9—Simulated component concentrations at 0.33 HCPVI for the quaternary displacement at 700 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.

The tie-lines in the two-phase regions on the upstream and downstream sides also show their immiscibilities.

Figs. 9 through 12 show the profiles of component concentrations, phase mole fractions, phase saturations, and phase densities, respectively, at 0.33 HCPVI at 700 psia. In Fig. 9, the PC4 concentration is significantly reduced at the three-phase leading edge, and the PC3 concentration becomes essentially zero in the threephase region. As a result, the tie triangle at the three-phase trailing edge is on the PC3-free ternary subsystem, which is shown in Fig. 5. The amount of the  $L_1$  phase rapidly decreases at the three-phase leading edge in Figs. 10 and 11. The efficient oil displacement is achieved because of the high concentration of the denser injection component PC2 in the three-phase region, as shown in Fig. 9. Fig. 12 shows that the densities of the  $L_1$  and  $L_2$  phases are close to each other at the three-phase leading edge. However, these two phases are still away from each other in composition space with a distance of 0.0547 in Fig. 8.

Fig. 13 shows the profiles of fractional flow at 0.33 HCPVI at 700 psia. The  $L_2$  phase has high fractional-flow values upstream of the three-phase leading edge, indicating that the  $L_2$  phase plays an important role in transport of solvent components during the displacement. Fig. 14 presents the overall molar flow  $\sum$  $\eta_{j=1} \rho_j x_{ij} f_j$  for component i, where  $\rho_j$  is the molar density of phase j,  $x_{ij}$  is the concentration of component i in phase j, and  $f_j$  is the fractional flow of phase j. The overall molar flow of PC2 is higher than that of PC1 upstream of the three-phase leading edge. The fast propagation of



Fig. 11—Simulated phase saturations at 0.33 HCPVI for the quaternary displacement at 700 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 12—Simulated phase densities at 0.33 HCPVI for the quaternary displacement at 700 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 14—Simulated overall molar flow for each component at 0.33 HCPVI for the quaternary displacement at 700 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.

the denser injection component yields efficient oil displacement by rich gas, as presented in Fig. 9.

Fig. 15 gives the composition path in the quaternary diagram at 1,000 psia. Figs. 16 through 19 show the profiles of component



Fig. 16—Simulated component concentrations at 0.33 HCPVI for the quaternary displacement at 1,000 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 13—Simulated phase fractional flow for each phase at 0.33 HCPVI for the quaternary displacement at 700 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 15—Phase behavior along the composition path in the quaternary displacement at 1,000 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2. A few tie-lines are shown in the upstream two-phase region and in the downstream twophase region. A few tie triangles are shown in the three-phase region to show a continuous variation between the leading and trailing edges of the three-phase region.



Fig. 17—Simulated phase mole fractions at 0.33 HCPVI for the quaternary displacement at 1,000 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 18—Simulated phase densities at 0.33 HCPVI for the quaternary displacement at 1,000 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 20—Phase behavior along the composition path in the quaternary displacement at 1,750 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2. A few tie-lines are shown in the upstream two-phase region and in the downstream twophase region. A few tie triangles are shown in the three-phase region to show a continuous variation between the leading and trailing edges of the three-phase region.



Fig. 22—Simulated phase molar fractions at 0.33 HCPVI for the quaternary displacement at 1,750 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 19—Simulated overall molar flow for each component at 0.33 HCPVI for the quaternary displacement at 1,000 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 21—Simulated component concentrations at 0.33 HCPVI for the quaternary displacement at 1,750 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.

concentrations, phase mole fractions, phase densities, and overall molar flows, respectively, at 0.33 HCPVI at 1,000 psia. The same set of figures is given for the displacement at 1,750 psia in Figs. 20 through 24. The displacement of PC4 at the three-phase leading edge becomes less efficient with increasing pressure as shown in Figs. 9, 16, and 21. Also, the PC3 concentration upstream of the trailing edge of the three-phase region increases with increasing pressure. Consequently, the tie triangle at the three-phase trailing edge is detached from the PC3-free ternary subsystem in Figs. 15 and 20. Fig. 22 clearly shows the less efficient oil displacement at 1,750 psia compared with Figs. 10 and 17.

The decreasing miscibility level with increasing pressure can be qualitatively seen in density profiles in Figs. 12, 18, and 23. Figs. 20 and 23 indicate that the three-phase equilibria simulated in the displacement at 1,750 psia are not close to CEP tie-lines. The  $L_2$  phase is important in transporting solvent components, as shown in Fig. 13. However, Figs. 14, 19, and 24 show that the overall molar flow of PC2 becomes lower compared with that of PC1 in the three-phase region as pressure increases. The solvent that contacts the  $L_1$  phase at the three-phase leading edge becomes leaner as pressure increases. This solvent propagation behavior with respect to pressure not only reduces the level of miscibility between the  $L_1$  and  $L_2$  phases, but also makes the propagation of the three-phase region faster. Figs. 10 and 22 clearly show the difference in propagation rates of three phases at 700 and 1,750 psia.



Fig. 23—Simulated phase densities at 0.33 HCPVI for the quaternary displacement at 1,750 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.

At 2,500 psia, three phases are not present, and the  $L_2$  phase displaces the oil. This immiscible two-phase flow results in a low displacement efficiency of 59.27% at 2.0 HCPVI. The oil recovery decreases when the three-phase region disappears as pressure increases (Fig. 7).

As mentioned previously, the nonmonotonic trend of oil recovery at a given throughput occurs when the local oil displacement by three hydrocarbon phases becomes less efficient with increasing pressure in the cases considered in this section. The next section, Mass Transfer on Multiphase Transitions, presents simple conditions to quantify the local displacement efficiency by three hydrocarbon phases on the basis of mass conservation for multiphase transitions.

Relative permeability models can significantly affect predictions of solvent-injection processes. Various relative permeability models were tested for simulation of solvent injection for Alaskan heavy oils (Mohanty et al. 1995; Wang and Strycker 2000; Guler et al. 2001; Li et al. 2003; Aghbash and Ahmadi 2012). Guler et al. (2001) showed that the simulation results were sensitive to the relative permeability parameters regardless of which relative permeability model was used. As shown in the figure in Appendix A, the  $L_2$  phase is the intermediate phase that can change the composition between the equilibrium  $L_1$  and V phases. To see the effect of the  $L_2$ -phase relative permeability parameters on the quaternary oil re-



Fig. 24—Simulated overall molar flow for each component at 0.33 HCPVI for the quaternary displacement at 1,750 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.

covery, simulations are repeated at 1,000 and 1,750 psia with the injection gas consisting of 20% PC1 and 80% PC2, where the relative permeability parameters for the  $L_2$  phase are set to be the same as those for the  $L_1$  phase (Table 3). Figs. 25 through 28 show the profiles of component concentrations and phase mole fractions at 0.33 HCPVI at 1,000 and 1,750 psia. The three-phase region propagates slower than the original cases. The effect is more significant at 1,750 psia because the displacement is more immiscible at 1,750 psia than at 1,000 psia. With the modified relative permeability parameters, the oil recovery at 2.0 HCPVI is calculated to be 79.76 and 68.53% at 1,000 and 1750 psia, respectively.

As discussed in the Introduction, gravity segregation and front instability must be taken into account when reservoir-flow patterns of solvent injection are concerned. In Figs. 12, 18, and 23, density differences between the  $L_1$  and  $L_2$  phases are small as also observed by Guler et al. (2001) and Wang et al. (2003). These authors showed that gravity segregation in oil displacement by the  $L_2$  phase in multidimensional simulations was less significant than expected from conventional gas injection. Fig. 29 compares total relative mobility in the quaternary oil displacements at different pressures at 0.33 HCPVI. As expected, the displacement becomes less unstable as the level of miscibility decreases with increasing pressure. Similar simulation results were presented in Mohanty et al. (1995).



Fig. 25—Simulated component concentrations at 0.33 HCPVI for the quaternary displacement at 1,000 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2. The relative permeability parameters for the  $L_2$  phase are set to be the same as those for the  $L_1$  phase.



Fig. 26—Simulated phase mole fractions at 0.33 HCPVI for the quaternary displacement at 1,000 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2. The relative permeability parameters for the  $L_2$  phase are set to be the same as those for the  $L_1$  phase.



Fig. 27—Simulated component concentrations at 0.33 HCPVI for the quaternary displacement at 1,750 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2. The relative permeability parameters for the  $L_2$  phase are set to be the same as those for the  $L_1$  phase.

An approximate Péclet number is 2,000 for the 1D quaternary displacements described previously, where the IMPEC simulator was used with 1,000 equally spaced gridblocks and small timestep sizes [see Johns et al. (2000) for an explanation of the approximation]. As explained in Jessen et al. (2004), numerical dispersion can significantly affect simulation results for oil displacement by gas. The quaternary displacements at 1,000 and 1,750 psia were repeated with two different numerical-dispersion levels, one with 250 gridblocks and the other with 50 gridblocks. They correspond to approximate Péclet numbers of 500 and 100, respectively. In the displacements at 1,000 psia, oil recoveries simulated at 2.0 HCPVI are 78.39% with 1,000 gridblocks, 72.24% with 250 gridblocks, and 59.24% with 50 gridblocks. In the displacements at 1,750 psia, they are 62.30% with 1,000 gridblocks, 60.65% with 250 gridblocks, and 55.03% with 50 gridblocks. The effect of numerical dispersion is more significant at 1,000 psia than at 1,750 psia because the level of miscibility is higher at 1,000 psia, as described previously in this section. A sensitivity study of simulation results to numerical dispersion can be also found in Okuno (2009) for low-temperature  $CO<sub>2</sub>$  floods involving three-hydrocarbon-phase behavior.



Fig. 29—Simulated total relative mobility at 0.33 HCPVI for the quaternary displacements at 700, 800, 1,000, 1,500, and 1,750 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2.



Fig. 28—Simulated phase mole fractions at 0.33 HCPVI for the quaternary displacement at 1,750 psia at 86<sup>º</sup> F. The oil and gas properties are given in Tables 1 and 2. The relative permeability parameters for the  $L_2$  phase are set to be the same as those for the  $L_1$  phase.

#### Mass Transfer on Multiphase Transitions

Our investigation in this section is focused on phase transitions between two and three phases in three-hydrocarbon-phase displacement. An analysis of mass conservation is presented for multiphase transitions in three-hydrocarbon-phase displacements. Material-balance equations for 1D dispersion-free compositional flow are discretized in Appendix B for a multiphase transition between  $N_P^U$  and  $N_P^D$  phases, where  $N_P^U$  and  $N_P^D$  are the numbers of phases on the upstream and downstream sides, respectively. The resulting equation (Eq. B-5) is of the identical form with the generalized jump conditions (Eq. B-7), which can be used in the MOC solution of multiphase flow. Eq. B-5 is more general than Eq. B-7, and can be used to analyze interphase mass transfer on multiphase transitions in the presence of numerical dispersion.

Eqs. B-5 and B-7 state that a multiphase transition between  $N_P^U$ and  $\overrightarrow{N_P}$  phases occurs through an intersection between the extensions of the two tie simplexes defined by  $\underline{x}_j^U$  ( $j = 1, 2, ..., N_P^U$ ) and  $\underline{x}_k^D$  ( $k = 1, 2, \dots, N_P^D$ ), where  $\underline{x}_j$  is the composition of equilibrium phase j. For a phase transition between one and two phases with a shock, this statement reduces to the well-known result of Helfferich (1981)—that a shock between one and two phases must occur on the tie-line extension. A phase transition between two and three phases occurs through an intersection between the tie-line extension and the tie-triangle-extension plane. Redistribution of components on the phase transition then satisfies the material balance for the two and three phases.

The phase labeling given in Fig. 1 is used to discuss an efficient redistribution of components on multiphase transition. The two nonoleic phases are partially miscible with the  $L_1$  phase in the three-phase displacements studied in this research. However, the two nonoleic phases can collectively achieve high displacement efficiency if two conditions are satisfied on the phase transitions between two and three phases. The first condition is that the appearance of the  $N_2$  phase should occur by splitting the  $L_1$  phase in the downstream two-phase region into the  $L_1$  and  $N_2$  phases in the three-phase region. The second condition is that the  $N_1$  and  $N_2$ phases in the three-phase region should merge into the  $N_3$  phase in the upstream two-phase region.

It is easy to derive mathematical expressions for these conditions. For instance, derivation for the first condition starts with Eq. B-5 for the leading edge of the three-phase region [i.e.,  $\sum_{j} \gamma_j^U \underline{c}_j^U = \sum_{k} \gamma_k^D \underline{c}_k^D$ , where  $j = (L_1, N_1, N_2)$  and  $k = (L_1, N_1)$ . The first condition is

$$
\left\|\gamma_{N_1}^U \underline{c}_{N_1}^U - \gamma_{N_1}^D \underline{c}_{N_1}^D\right\|_2 < \varepsilon, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \tag{1}
$$



Fig. 30—Schematic of phase transition in composition space at the leading edge of the three-phase region. It is assumed that there are  $L_1$  and V downstream, and  $L_1$ ,  $L_2$ , and V upstream of the phase transition. Black dots indicate equilibrium phase compositions. The superscripts  $D$  and  $U$  stand for downstream and upstream, respectively. Redistribution of components between two and three phases occurs through the intersection. The composition of the  $P_1$  pseudophase is defined where the line connecting the intersection and the  $V^U$  phase composition intersects (the extension of) the  $L_1/L_2$  edge of the tie triangle.

such that

$$
\gamma_{N_2}^U \underline{c}_{N_2}^U + \gamma_{L_1}^U \underline{c}_{L_1}^U \approx \gamma_{L_1}^D \underline{c}_{L_1}^D \quad \dots \dots \dots \dots \dots \dots \dots \dots \tag{2}
$$

Substitution of Eq. 1 into Eq. B-5 yields Eq. 2. Eq. 2 states that redistribution of components must occur between the  $L_1$  and  $N_2$  phases. Similarly, the second condition is

$$
\left\|\gamma_{L_1}^D \underline{c}_{L_1}^D - \gamma_{L_1}^U \underline{c}_{L_1}^U\right\|_2 < \varepsilon, \quad \ldots \tag{3}
$$

such that

$$
\gamma_{N_1}^D \underline{c}_{N_1}^D + \gamma_{N_2}^D \underline{c}_{N_2}^D \approx \gamma_{N_3}^U \underline{c}_{N_3}^U. \quad \dots \dots \dots \dots \dots \dots \dots \tag{4}
$$

Summation of Eqs. 3 and 4 yields Eq. B-5 for the trailing edge of the three-phase region. Eq. 4 states that the two nonoleic phases in the three-phase region should merge into a nonoleic phase in the upstream two-phase region.

Eqs. 1 and 3 can be rewritten by use of phase compositions as follows:

$$
\delta^L = \left\|\Gamma_{N_1}^U \underline{x}_{N_1}^U - \Gamma_{N_1}^D \underline{x}_{N_1}^D\right\|_2 < \varepsilon, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5)
$$

$$
\delta^T = \left\| \Gamma_{L_1}^U \underline{x}_{L_1}^U - \Gamma_{L_1}^D \underline{x}_{L_1}^D \right\|_2 < \varepsilon. \quad \dots \dots \dots \dots \dots \dots \dots \tag{6}
$$

The  $\Gamma_i$  (  $j = 1, 2,..., N_P$ ) parameters determine the relative location of the  $N_P$ -phase tie simplex and an intersection involved in the phase transition. The conditions specific to the quaternary displacements in the previous section are as follows:  $\delta^L =$  $\left\|\Gamma_{V}^{U}\underline{\mathbf{x}}_{V}^{U}-\Gamma_{V}\underline{\mathbf{x}}_{V}^{D}\right\|_{2} < \varepsilon$  and  $\delta^{T} = \left\|\Gamma_{L_{1}}^{U}\underline{\mathbf{x}}_{L_{1}}^{U}-\Gamma_{L_{1}}^{D}\underline{\mathbf{x}}_{L_{1}}^{D}\right\|_{2}$  $\left\|\Gamma_{L_1}^U \underline{x}_{L_1}^U - \Gamma_{L_1}^D \underline{x}_{L_1}^D\right\|_2 < \varepsilon$ . Figs. 30 and 31 give schematics for the phase transitions at the leading and trailing edges of the three-phase region, respectively. These schematics indicate that a phase transition between two and three phases involves an intersection of the tie-line extension and the tie-triangle extension as described in Appendix B.

Once the tie-line and tie triangle involved in a phase transition (e.g., the tie-line downstream and the tie triangle upstream in Fig. 30) are given, we can calculate an intersection of them. The location of the intersection relative to the tie-line then gives the  $\Gamma_i$  $(j = V \text{ and } L_1)$  parameters on the tie-line extension. Thus,  $\underline{z}^{\text{int}} = \Gamma_{V}^{D} \underline{x}_{V}^{D} + \Gamma_{L_1}^{D} \underline{x}_{L_1}^{D}$ , where  $\Gamma_{V}^{D} + \Gamma_{L_1}^{D} = 1.0$  and  $\underline{z}^{\text{int}}$  is the intersection composition. Similarly, the location of the same intersection relative to the tie triangle gives the  $\Gamma_j$  ( $j = V, L_1$ , and  $L_2$ ) parameters on the tie-triangle extension. Thus,  $\underline{z}^{\text{int}} = \Gamma V \underline{x}^U V +$  $\Gamma_{L_1}^U \underline{x}_{L_1}^U + \Gamma_{L_2}^U \underline{x}_{L_2}^U$ , where  $\Gamma_V^U + \Gamma_{L_1}^U + \Gamma_{L_2}^U = 1.0$ . Calculation of  $\delta^L$ and  $\delta^T$  will be conducted by use of this procedure for the quaternary displacements later in this section, and for the West Sak oil displacements in the subsequent section.

Fig. 30 shows a pseudophase  $P_1$ , where the line connecting the intersection and the  $V^U$  phase composition intersects (the extension of) the  $L_1/L_2$  edge of the tie triangle. We can consider that redistribution of components from two to three phases occurs in



Fig. 31—Schematic of phase transition in composition space at the trailing edge of the three-phase region. It is assumed that there are  $L_1$  and  $L_2$  upstream, and  $L_1$ ,  $L_2$ , and V downstream of the phase transition. Black dots indicate equilibrium phase compositions. The superscripts D and U stand for downstream and upstream, respectively. Redistribution of components between two and three phases occurs through the intersection. The composition of the  $P_2$  pseudophase is defined where the line connecting the intersection and the  $L_1^D$  phase composition intersects (the extension of) the  $V/L<sub>2</sub>$  edge of the tie triangle.

three steps: the  $L_1$  and V phases on the downstream tie-line form the intersection composition; the intersection composition forms two phases, the  $P_1$  and V phases, on the upstream tie triangle; and the  $P_1$  phase splits into the  $L_1$  and  $L_2$  phases on the tie triangle. Fig. 31 shows a pseudophase  $P_2$ , where the line connecting the intersection and the  $L_1$  phase composition intersects the extension of the  $L_2/V$  edge of the tie triangle. Redistribution of components from three to two phases occurs in the following three steps: the  $L_2$  and V phases form the  $P_2$  phase on the tie-triangle extension downstream; the  $P_2$  and  $L_1$  phases form the intersection composition; and the intersection composition forms the  $L_1$  and V phases on the tie-line upstream. Fig. 31 shows a more general case, where the pseudophase is outside the tie triangle.

Eqs. 2 and 4 become exact when the pseudotie-line on the tie triangle and the tie-line coincide. In Fig. 30, for example, the  $L_1^U$ and  $\tilde{L}_2^U$  phases on the tie triangle merge into the  $L_1^D$  phase on the tie-line without affecting the other coexisting V phase when the  $P_1/V^U$  pseudotie-line and the  $L_1^D/V^D$  tie-line coincide. This can occur for phase transitions on a CEP tie-line and on an edge of a tie triangle. LaForce and Orr (2009) presented the latter type of phase transitions in analytical solutions for oil displacements, which cross the boundary between two and three phases without a shock.

The efficient mass transfer on multiphase transitions near the UCEP and LCEP tie-lies was described for low-temperature  $CO<sub>2</sub>$ floods in Okuno et al. (2011). This can be interpreted by use of the limiting case mentioned previously. As the LCEP is approached in Fig. 30, the  $L_1$  and  $L_2$  phases on the upstream tie triangle become closer to each other. The  $P_1/V$  pseudotie-line then becomes closer to the  $L_1/V$  tie-line downstream. Similarly, the  $P_2/$  $L_1$  pseudotie-line becomes closer to the upstream  $L_1/L_2$  tie line when the composition path goes near the UCEP tie-line. Eqs. 5 and 6 are naturally satisfied with small  $\varepsilon$  values for such low-temperature  $CO<sub>2</sub>$  floods. However, this does not occur for the efficient displacements by use of the quaternary system in the previous section. For example, Fig. 15 shows tie triangles along the composition path that are not close to CEP tie-lines.

We calculate the distances given in Eqs. 5 and 6 (i.e.,  $\delta^L =$  $\|\Gamma_{N_1}^U \underline{x}_N^U$  $\frac{U}{N_1} - \Gamma_{N_1}^D \underline{x}_{N_1}^D \|_2$  and  $\delta^T = \| \Gamma_{L_1}^U \underline{x}_{L_1}^U\|_2$  $\sum_{L_1}^{U} - \Gamma_{L_1}^{D} \underline{x}_{L_1}^{D} \|_2$ ) for the quaternary displacements at 700, 800, 1,000, 1,500, and 1,750 psia. Fig. 32 shows that  $\delta^L$  and  $\delta^T$  decrease as pressure decreases for these displacements; that is, mass transfer on multiphase transitions occurs most efficiently at 700 psia. The  $L_1$  phase in the leading two-phase region splits into the  $L_1$  and  $L_2$  phases in the three-phase region, and the  $L_2$  and V phases in the three-phase region merge efficiently into the  $L_2$  phase in the trailing two-phase region. Consequently, the oil recovery at the breakthrough of the three-phase trailing edge exhibits the highest efficiency at 700 psia in Fig. 7.

The distances,  $\delta^L$  and  $\delta^T$ , are also calculated for quaternary displacements with different gas-enrichment levels. Injection gas consists of PC1 and PC2, but different levels of gas enrichment use different mixing ratios. Reservoir properties are given in Table 3. The displacement pressure is 1,500 psia, and the reservoir



Fig. 32—The distance parameters  $\delta^L$  and  $\delta^T$  (Eqs. 5 and 6) calculated for the quaternary displacements at 700, 800, 1,000, 1,500, and 1,750 psia. For these displacements, local displacement by three phases becomes more efficient for lower pressure. Oil recovery at breakthrough of the three-phase trailing edge is 78.42% at 700 psia, 78.37% at 800 psia, 78.30% at 1,000 psia, 68.86% at 1,500 psia, and 59.21% at 1,750 psia, as shown in Fig. 7.

temperature is 86°F. Three phases are present for displacements with high enrichment levels. Fig. 33 presents that local displacement by three phases becomes more efficient with decreasing enrichment. At 40% PC1,  $\delta^L$  is  $1.3 \times 10^{-2}$  and  $\delta^T$  is  $2.5 \times 10^{-4}$ . Fig. 34 shows that displacement efficiency at 2.0 HCPVI exhibits a maximum of 68.39% for the PC1 concentration of 20% in the injection gas. Three-phase displacement with less enrichment achieves higher local displacement efficiency, but it becomes slower. The trailing edge of three phases reaches the outlet at 0.709 HCPVI at 5% PC1, 0.724 HCPVI at 20% PC1, and 0.768 HCPVI at 40% PC1. The three-phase region is also present at 60% PC1, but its propagation is extremely slow. Oil recovery at a given throughput depends not only on local displacement efficiency by three phases, but also on the propagation rate of three phases. A maximum oil recovery at 2.0 HCPVI in Fig. 34 is a



Fig. 34—Oil recovery simulated for the quaternary displacements at different gas-enrichment levels at 1,500 psia and 86<sup>º</sup> F. The fluid properties are given in Tables 1 and 2. A maximum of 68.39% is observed for recovery at 2.0 HCPVI at a PC1 concentration of 20%. The trailing edge of the three-phase region reaches the outlet at 0.709 HCPVI at 5% PC1, 0.724 HCPVI at 20% PC1, and 0.768 HCPVI at 40% PC1. Oil recovery at breakthrough of the three-phase trailing edge is 65.2% at 5% PC1, 66.8% at 20% PC1, and 66.9% at 40% PC1. Oil displacement by three phases is more efficient, but slower, with increasing PC1 dilution. The three-phase region is also present at 60% PC1, but its propagation is extremely slow.



Fig. 33—The distance parameters  $\delta^L$  and  $\delta^T$  (Eqs. 5 and 6) calculated for the quaternary displacements at different enrichment levels at 1,500 psia and 86<sup>º</sup> F. For these displacements, local displacement by three phases becomes more efficient for higher PC1 dilution. Oil recovery at breakthrough of the threephase trailing edge is 65.2% at 5% PC1, 66.8% at 20% PC1, and 66.9% at 40% PC1, as shown in Fig. 34.

result of the balance between the local displacement efficiency and the propagation rate of three hydrocarbon phases.

### Case Study for West Sak Oil Displacement With Enriched Gas

Nonmonotonic oil recovery at a given throughput with respect to gas enrichment has been reported for the West Sak oil displacement (DeRuiter et al. 1994; Mohanty et al. 1995). However, its detailed mechanism is uncertain in the literature, as mentioned in the Introduction. In this section, the distance conditions derived in the preceding section are applied to the West Sak oil displacement with enriched gas.

The West Sak oil is characterized by use of the Peng-Robinson EOS on the basis of data available in Okuyiga (1992) (Xu 2012). The 15-component model given in Table 4 includes eight pseudocomponents for the  $C_{7+}$  fraction. The Lohrenz-Bray-Clark model (Lohrenz et al. 1964) is used for viscosity calculations. The oil gravity is calculated to be approximately  $21^{\circ}$ API. Fig. 35 presents the P/T diagram for the oil. The saturation pressure is 1,197 psia at the reservoir temperature of 65°F.

The injection gas consists of two gaseous mixtures: the richgas mixture of 35 mol% ethane, 34 mol% propane, and 31 mol% *n*-butane, and the lean-gas mixture of 84 mol%  $C_1$ , 9 mol% ethane, 6 mol% propane, and 1 mol% *n*-butane. Oil displacements are simulated for eight different enrichment levels. The resulting enriched gases are referred to by use of their  $C_1$  concentrations. Fig. 36 shows the pressure/solvent-mole-fraction diagram for the reservoir oil and the injection gas with  $60\%$  C<sub>1</sub> concentration at 65-F. Three phases are present at high solvent concentrations at the operating pressure range. The  $L_1/L_2$  immiscibility persists to high pressure. The reservoir properties used are given in Table 3. The displacement pressure is 1,500 psia.

As mentioned in the Introduction, three-phase behavior bounded by CEPs has been observed for *n*-alkane binaries;  $C_1/$  $nC_6$ ,  $C_1/nC_7$ ,  $C_2/n$ -alkanes from  $nC_{18}$  to  $nC_{25}$ ; and  $C_3/n$ -alkanes heavier than  $nC_{30}$ . Mixtures of the rich-gas components—C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>—likely tend to cause three-phase behavior with the  $C_{7+}$ fraction of the oil at reservoir temperatures.

Fig. 37 presents oil recovery at different gas enrichments at 1.0, 1.5, and 2.0 HCPVI. Three hydrocarbon phases are present in the displacements at  $C_1$  concentrations in the injection gas between 50 and 70%. At a  $C_1$  concentration of 53%, oil recovery is 84.29% at 1.0 HCPVI, 90.18% at 1.5 HCPVI, and 91.53% at 2.0 HCPVI. The injection gas with this  $C_1$  concentration yields an optimum displacement for a fixed throughput in Fig. 37. Mohanty



et al. (1995) showed nonmonotonic recovery trends that are more obvious in their slimtube experiments and numerical simulations.

Fig. 38 shows the distances given in Eqs. 5 and 6 for the displacements at 50, 53, 55, and 60%  $C_1$  concentrations. The distances decrease for leaner injection gas. At the  $C_1$  concentration of 60%,  $\delta^L$  is  $9.0 \times 10^{-3}$  and  $\delta^T$  is  $3.9 \times 10^{-4}$ . These results indicate that the local displacement by three hydrocarbon phases becomes more efficient with decreasing gas enrichment. The injection gas with the  $C_1$  concentration of 60% gives the maximum efficiency of three-phase local displacement (Fig. 37). Oil recovery at breakthrough of the three-phase trailing edge is  $90.4\%$  at  $50\%$  C<sub>1</sub>, 92.0% at 53%  $C_1$ , and 97.4% at 60%  $C_1$ .

However, propagation of three phases is slower at higher  $C_1$ concentrations. The trailing edge of three phases reaches the outlet at 2.15, 2.34, 2.73, and 14.94 HCPVI at the  $C_1$  concentrations of 50, 53, 55, and 60%, respectively. We could not observe the three-phase trailing edge at the outlet for the  $C_1$  concentration of 70%. Because of the slow propagation of three phases, oil recovery is 69.01% at 1.0 HCPVI, 85.71% at 1.5 HCPVI, and 87.75% at 2.0 HCPVI at the  $C_1$  concentration of 60%.

Local displacement by three phases is more efficient, but propagation of three phases is slower, for leaner injection gas for these three-phase displacements. These two factors determine a maximum in oil recovery at a given throughput in Fig. 37. A maximum



Fig. 35—P/T diagram of the West Sak oil given in Table 4. The Peng-Robinson EOS is used. The saturation pressure is 1,197 psia at the reservoir temperature of 65<sup>º</sup> F.

recovery at a given throughput will occur at a different dilution level when different reservoir and/or fluid properties are used.

# Conclusions

We investigated local efficiency of three-hydrocarbon-phase displacement of oil. Mathematical conditions were derived for efficient redistribution of components on multiphase transitions be tween two and three phases. These conditions were used to explain nonmonotonic oil recovery at a given throughput with respect to gas enrichment, which has been reported for the West Sak oil in the literature. Conclusions are as follows:

- Oil recovery in a PM displacement depends on two factors: local displacement efficiency and component propagation rates. Nonmonotonic oil recovery at a given throughput can occur when local displacement by three hydrocarbon phases becomes more efficient, but slower, with decreasing pressure or decreasing gas enrichment. This was confirmed by use of fine-scale simulations of quaternary displacements and the West Sak oil displacements. A maximum in oil recovery at a given throughput occurs as a consequence of the balance between the local displacement efficiency and the propagation rate of three hydrocarbon phases.
- Local displacement efficiency by three hydrocarbon phases depends significantly on how components are redistributed on



Fig. 36-Pressure/solvent-mole-fraction diagram at 65°F for mixtures of the West Sak oil and the injection gas with  $60\%$  C<sub>1</sub>. Fluid properties used are given in Table 4. The oleic, solvent-rich-liquid, and gaseous phases are given as  $L_1$ ,  $L_2$ , and V, respectively.



Fig. 37—Oil recovery simulated for the West Sak displacements at different gas-enrichment levels at 1,500 psia and 65<sup>º</sup> F. The fluid properties are given in Table 4. A maximum of 91.53% is observed for recovery at 2.0 HCPVI at a  $C_1$  concentration of 53%. The trailing edge of the three-phase region reaches the outlet at 2.15 HCPVI at 50%  ${\sf C}_1,$  2.34 HCPVI at 53%  ${\sf C}_1,$  2.73 HCPVI at 55%  ${\sf C}_1$ , and 14.94 HCPVI at 60%  ${\sf C}_1.$  Oil recovery at breakthrough of the three-phase trailing edge reaches 97.4% at  $60\%$  C<sub>1</sub>. Oil displacement by three phases is more efficient, but slower, with decreasing gas enrichment.

multiphase transitions between two and three phases. At the leading edge of the three-phase region, the second nonoleic phase should appear from the oleic phase of the downstream two-phase region. At the trailing edge of the three-phase region, two nonoleic phases of the three-phase region should merge into the nonoleic phase of the upstream two-phase region.

- The distances defined in Eqs. 5 and 6 for efficient multiphase transitions can correctly identify the local displacement efficiency by three hydrocarbon phases. The distances were successfully used to explain the quaternary displacements and the West Sak oil displacements that exhibit nonmonotonic oil recovery. The distance conditions can also explain the efficient displacement through near-CEP behaviors presented in prior research on low-temperature  $CO<sub>2</sub>$  floods.
- Partially miscible displacement of oil by two nonoleic phases can be collectively efficient, even if they are individually immiscible with oil. The West Sak oil displacement with enriched gas studied in this research showed a displacement efficiency of 84.29% at 1.0 HCPVI, 90.18% at 1.5 HCPVI, and 91.53% at 2.0 HCPVI at 53%-C<sub>1</sub> dilution. With this C<sub>1</sub> dilution, the threephase displacement was locally efficient and fast enough to exhibit a high oil recovery.
- Mass conservation was analyzed for multiphase transitions in 1D oil displacement. Results showed that redistribution of components on a phase transition between  $N_P^U$  and  $N_P^D$  phases must occur through an intersection of the  $N_P^U$ -phase tie-simplex extension and the  $N_P^D$ -phase tie-simplex extension.  $N_P^U$  and  $N_P^D$ are the numbers of phases upstream and downstream of the phase transition, respectively.

#### Nomenclature

- $c_{ii}$  = volumetric fraction of component *i* in phase *j*
- $c_j$  = vector consisting of  $c_{ij}$  as defined in Eq. B-4
- $C_i$  = overall volume fraction of component *i*
- $f_i$  = fractional flow of phase j
- $\tilde{F}_i$  = overall fractional flow of component *i*
- $L_1$  = oleic phase
- $L_2$  = solvent-rich liquid phase
- $N_i$  ( $j=1, 2,$  or 3) = nonoleic phase (i.e.,  $L_2$  or V)
	- $N_C$  = number of components
	- $N_P$  = number of phases



Fig. 38—The distance parameters  $\delta^L$  and  $\delta^T$  (Eqs. 5 and 6) calculated for the West Sak displacements at different enrichment levels at 1,500 psia and 65<sup>º</sup> F. For these displacements, local displacement by three phases becomes more efficient for less gas enrichment. Oil recovery at breakthrough of the threephase trailing edge is 90.4% at 50%  $C_1$ , 92.0% at 53%  $C_1$ , and 97.4% at 60%  $C_1$ , as shown in Fig. 37.

 $P_C$  = critical pressure  $S_i$  = saturation of phase j  $T_C$  = critical temperature  $t_D =$  dimensionless time in PV  $V =$  gaseous phase  $V_C$  = critical volume  $x_D$  = dimensionless distance from the injector  $x_i$  = vector consisting of  $x_{ij}$  $x_{ij}$  = mole fraction of component *i* in phase *j*  $z^{\text{ini}}$  = intersection composition  $\gamma$  = parameter defined in Eq. B-5  $\dot{\Gamma}$  = parameter defined in Eqs. 5 and 6  $\delta$  = distance defined in Eqs. 5 and 6  $\varepsilon$  = small values used in Eqs. 1, 3, 5, and 6  $\Lambda =$  dimensionless shock velocity

#### **Superscripts**

$$
D =
$$
Downstream

 $U =$  Upstream

#### Acknowledgments

This research was partly supported by research grants from the Natural Sciences and Engineering Council of Canada (No. RGPIN 418266) and Japan Petroleum Exploration Company. Ryosuke Okuno was awarded the SPE Petroleum Engineering Junior Faculty Research Initiation Award. Zhongguo Xu has received a scholarship from the China Scholarship Council. We gratefully acknowledge these supports. We also thank Kamy Sepehrnoori for providing the UTCOMP simulator. Flow simulations in this research were conducted by use of the computational facility of Compute Canada.

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# Appendix A—Schematic of a Three-Phase Region Bounded by CEP Tie-Lines

A three-phase region has one degree of freedom at a given temperature and pressure for four components. Therefore, a threephase region is a volumetric region in a quaternary diagram. The three-phase region consists of an infinite number of tie triangles. A tie triangle changes its shape and size within the three-phase region. Two tie triangles are shown to illustrate tie triangles exhibiting near-CEP behavior. A CEP is not a point in composition space, but is a tie-line where two of the three phases are critical in the presence of the other noncritical phase. More details on three-hydrocarbon-phase behavior are given in Okuno (2009).



 $\circ$  Merging point of L<sub>1</sub> and L<sub>2</sub> phase compositions

Fig. A-1—Schematic of a three-phase region bounded by CEP tielines for a quaternary system at a fixed temperature and pressure.

# Appendix B—Mass Conservation on Multiphase **Transitions**

Conservation of mass for a component in  $N_P$ -phase flow through porous media is considered with the following assumptions:

- 1D flow with no gravity • Constant temperature
- Change in pressure is small over the displacement length
- Constant porosity with time
- No diffusion/dispersion
- No chemical reaction or sorption on the solid phase
- No capillary pressure
- Local equilibrium
- Ideal mixing
- Laminar flow
- We then obtain

$$
\frac{\partial C_i}{\partial t_D} + \frac{\partial F_i}{\partial x_D} = 0, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (B-1)
$$

where  $t_D$  is a dimensionless time measured in PV,  $x_D$  is a dimensionless distance from the injector,  $C_i$  is the overall volume fraction of component i,  $F_i$  is the overall fractional flow of component *i*, and *i* = 1, 2,...,  $(N_C - 1)$ .  $C_i$  and  $F_i$  are given as

$$
C_i = \sum_{j=1}^{N_P} S_j c_{ij}
$$

$$
F_i = \sum_{j=1}^{N_P} f_j c_{ij},
$$

where  $S_i$  is the saturation of phase j,  $f_i$  is the fractional flow of phase *j*, and  $c_{ij}$  is the volume fraction of component *i* in phase *j*. A detailed derivation of Eq. B-1 is given in Orr (2007).

The weak form of Eq. B-1 is

$$
\frac{\mathrm{d}}{\mathrm{d}t_D} \int C_i \mathrm{d}V + \int n \cdot F_i \mathrm{d}S = 0, \quad \dots \dots \dots \dots \dots \dots \dots \dots (B-2)
$$

where *V* and *S* are the volume and surface area of the control volume of interest, respectively.  $n$  is the outward normal unit vector on surface S. Let us consider two consecutive gridblocks in a 1D simulation model, where  $N_P^U$  and  $N_P^D$  phases are present in the upstream and downstream cells, respectively, at a given time. A uniform grid size of  $\Delta x_D$  is considered.

Suppose a phase transition between  $N_P^U$  and  $N_P^D$  propagates at a dimensionless velocity of  $v_D = \Delta x_D / \Delta t_D$ , where  $\Delta t_D$  is a certain time period in PV. Discretization of Eq. B-2 with  $\Delta x_D$  and  $\Delta t_D$  using the one-point upstream weighting for the flux term yields

$$
v_D = \frac{\Delta x_D}{\Delta t_D} = \frac{F_i^U - F_i^D}{C_i^U - C_i^D}.
$$
 (B-3)

Rearrangement of Eq. B-3 gives

$$
\sum_{j=1}^{N_p^U} \left( v_D S_j^U - f_j^U \right) c_j^U = \sum_{j=1}^{N_p^D} \left( v_D S_j^D - f_j^D \right) c_j^D, \quad \dots (B-4)
$$

where  $c_j$  is a vector consisting of  $c_{ij}$ . Dividing Eq. B-4 by ( $v_D$  – 1),

$$
\sum_{j=1}^{N_p^U} \gamma_j^U \underline{c}_j^U = \sum_{j=1}^{N_p^D} \gamma_j^D \underline{c}_j^D, \quad \dots \dots \dots \dots \dots \dots \dots \quad (B-5)
$$

where 
$$
\gamma_j^U = \frac{v_D S_j^U - f_j^U}{v_D - 1}
$$
 and  $\gamma_j^D = \frac{v_D S_j^D - f_j^D}{v_D - 1}$ . Note that  $\sum_{j=1}^{N_p^U} \gamma_j^U = 1.0$  and  $\sum_{j=1}^{N_p^D} \gamma_j^D = 1.0$ .

Components are redistributed on a multiphase transition. Eq. B-5 indicates that the redistribution of components must occur through an intersection of the  $N_P^U$ -phase tie-simplex extension and the  $\overline{N_P^D}$ -phase tie-simplex extension for the phase transition between the  $N_P^U$  and  $N_P^D$  phases. For example, a phase transition between two and three phases must occur through an intersection of the tie-line extension and the tie-triangle extension in composition space, as shown in Figs. 30 and 31.

A special case of multiphase transitions is a phase-transition shock in the MOC solution of Eq. B-1. The conservation equations for a shock are called the jump conditions. The jump conditions for a shock with a dimensionless velocity of  $\Lambda$  are

$$
\Lambda = \frac{F_i^U - F_i^D}{C_i^V - C_i^D}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(B-6)}
$$

where  $i = 1, 2, \dots, (N_C - 1)$ . Replacement of  $v_D$  in Eqs. B-4 and B-5 with  $\Lambda$  results in

$$
\sum\nolimits_{j=1}^{N_p^U} \gamma_j^U \underline{c}_j^U = \sum\nolimits_{j=1}^{N_p^D} \gamma_j^D \underline{c}_j^D, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (B-7)
$$

where  $\gamma_j^U = \frac{\Lambda S_j^U - f_j^U}{\Lambda - 1}$  and  $\gamma_j^D = \frac{\Lambda S_j^D - f_j^D}{\Lambda - 1}$ . Note that  $\sum_{j=1}^{N_p^U} \gamma_j^U =$ 1.0 and  $\sum_{j=1}^{N_P^D} \gamma_j^D = 1.0$ .

Eq. B-7 indicates that a shock must occur through an intersection of the tie-simplex extension of  $(N_P^D - 1)$  dimensions and that of  $(N_P^U - 1)$  dimensions. For  $(N_P^D, N_P^U) = (1, 2)$ , the previous result reduces to the well-known result of Helfferich (1981), that a shock between one and two phases must occur on the tie-line extension. For  $(N_P^D, N_P^U) = (2, 3)$ , a shock between two and three phases must occur through an intersection of the tie-triangleextension plane and the tie-line extension. Eq. B-5 is of the identical form with the generalized jump conditions on multiphase transition presented in Eq. B-7. The difference is that  $v_D$  in Eq. B-5 is in general not the same as the shock velocity  $\Lambda$  in Eq. B-7. Eq. B-5 is even more general, and applicable in mechanistic interpretation of mass transfer on a multiphase transition in the presence of numerical dispersion.

LaForce (2005) and LaForce and Johns (2005a, b) studied three-phase displacement of oil with three components. In their studies, composition paths are constrained to exist in composition space of two dimensions. A tie triangle and tie-lines are always on the 2D composition plane in their cases. The proof given here was neither needed nor presented in their research.

#### SI Metric Conversion Factors



\*Conversion factor is exact.

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