

EXPERIMENTAL STUDIES AND DISCRETE THERMODYNAMIC MODELING ON SUPERCRITICAL CO₂ EXTRACTIONS OF A HEXADECANE AND CRUDE OIL

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Abstract—Continuous multiple-contact experiments using a supercritical CO₂ were performed to study the phase equilibrium behavior of the dynamic extractions of a hexadecane and crude oil. The extraction yields increased as CO₂ density increased with a pressure rise at constant temperature. The rates of extractions were also greater at higher pressure. The simulated distillation analysis of extracted crude oil samples represented that the earlier extracts contained lighter compounds and the latter extracts contained progressively heavier compounds. These compositional changes occurring during a dynamic extraction were also ascertained by phase-equilibrium flash calculations using the equations of state and a pseudo-component lumping method. Two different equations of state, Soave-Redlich-Kwong and Peng-Robinson, were used to predict the equilibrium compositions of the extract phase that is a supercritical carbonic phase. The results of phase behavior calculations established the nature of the extraction and partitioning process as a function of time. These results also provided reasonable agreement between the experimental data and the calculated values.

Key words: SFE, Supercritical CO₂, Hexadecane, Crude Oil, Modeling, Phase Equilibrium Calculation, Pseudo-components, Lumping, EOS

INTRODUCTION

Prediction of phase equilibria of hydrocarbon mixtures with CO₂ is important for many applications [Brennecke and Eckert, 1989; Firoozabadi et al., 1988; Natakki, 1989; Orr et al., 1983; Turek, 1984]. This phase behavior investigation of hydrocarbon mixtures such as a crude oil has led to considerable activity in search for separation and/or extraction processes using supercritical fluids and numerical simulation of CO₂ enhanced oil recovery (EOR) processes [Ely and Baker, 1983; Holm and Josendal, 1974; Mulliken and Sandler, 1980; Mungan, 1981; Shelton and Yarborough, 1977]. One of the primary advantages of supercritical fluid extraction or separation in its applications is that the fluid density can be varied continuously from gas-like to liquid-like densities by changing the process variables such as pressure, temperature and time. Compared to liquid solvents, supercritical fluids have a high diffusivity and a low viscosity, which allow more rapid and effective extraction and phase separation. For the design of processes taking advantages of these preferential qualities of supercritical fluids, the model for a reliable description not only of phase equilibria but also of other thermodynamic properties has been established for several specific system [Brennecke and Eckert, 1989; Orr et al., 1983; Turek, 1984].

Cubic equation of state (EOS) provides one of the most popular methods for predicting fluid phase equilibria, and some of EOSs like the Soave-Redlich-Kwong [Soave, 1972] and the Peng-Robinson [1976] have been successfully used to describe two- and three-phase equilibria for the mixtures of CO₂ with complex hy-

drocarbons. For a complex hydrocarbon mixture system, one of the requirements of using these equations is that it requires mixing rules to relate pure component properties to mixture properties. The mixing rules used for the mixtures in this study are given below:

$$a = \sum_i \sum_j x_i x_j a_{ij} \text{ where } a_{ij} = (1 - \delta_{ij}) \sqrt{a_i a_j}, i \neq j \quad (1)$$

$$b = \sum_i x_i b_i \quad (2)$$

The binary interaction parameter, δ_{ij} , is an empirically determined coefficient characterizing the binary system formed by component i and component j , and the δ_{ij} is usually near zero between hydrocarbon components. For systems in which the correction is needed, δ_{ij} is approximately independent of temperature, pressure and composition. It is seldom possible to justify these rules theoretically and the empirical adjustment of the mixing rule equations has accounted for many papers in the literature [Katz and Firoozabadi, 1978; Mulliken and Sandler, 1980; Natakki, 1989; Turek, 1984].

THEORETICAL

1. Phase Equilibrium Calculation Procedure

Modeling of the extraction process requires consideration of equilibrium between the phases formed under experimental conditions conducted in this study. The basis for the two phase flash equilibrium calculation was a successive substitution (SS) method [Natakki, 1989; Ngheim et al., 1983], which consists of the following steps.

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(1) Assume equilibrium K values
 (2) Calculate the phase distribution and compositions corresponding to given K.

(3) Calculate component fugacities in each phase using an appropriate EOS and check for equality.

(4) If equality is not achieved, correct K values on the basis of the fugacities.

(5) Repeat the calculation beginning with step 2 until to get equality.

The material balance for component i in the flash process is given by

$$Fz_i = Lx_i + Vy_i \quad (3)$$

The equilibrium constant (K) is introduced in the conventional way:

$$K_i = \frac{y_i}{x_i} \quad (4)$$

Thus, above equations can be combined and expressed by the composition (y_i) of vapor phase as a function of the feed composition (z_i), the equilibrium constant (K_i) and the liquid mole fraction (L):

$$y_i = \frac{z_i}{1 + L\left(\frac{1}{K_i} - 1\right)} \quad (5)$$

In the iterative procedure, the fugacities are determined from the compositions and the K values are corrected using the fugacities before the calculations are repeated. The liquid and vapor fugacities can be written

$$f_{L,i} = x_i \phi_{L,i} P \quad (6)$$

$$f_{V,i} = y_i \phi_{V,i} P \quad (7)$$

where $f_{L,i}$ is fugacity of component i in the liquid phase, $f_{V,i}$ is fugacity of component i in the vapor phase, and $\phi_{L,i}$ and $\phi_{V,i}$ are the fugacity coefficients of component i. At equilibrium the fugacities for the vapor-liquid phases are equal and the equilibrium K-values are given by

$$f_{L,i} = f_{V,i} \quad (8)$$

$$K_i = \frac{y_i}{x_i} = \frac{\phi_{L,i}}{\phi_{V,i}} \quad (9)$$

The basic correction step in SS method is to use the last values for the fugacity coefficients to make an improved K value estimate.

2. Soave-Redlich-Kwong (SRK) EOS Model

Soave [1972] modified the Redlich-Kwong EOS to force a fit to saturation pressures of pure nonpolar and slightly polar substances, and proposed an equation of the form:

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)} \quad (10)$$

Above SRK EOS may be written in the following compressibility factor (Z) expression for single component i:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad (11)$$

$$\text{with } A = \frac{a_i P}{R^2 T^2} \text{ and } B = \frac{b_i P}{RT} \quad (12)$$

$$a_i = a_i \alpha_i \quad (13)$$

$$b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \quad (14)$$

$$\text{where } \alpha_i = 0.42747 \frac{R^2 T_{c,i}^2}{P_{c,i}} \quad (15)$$

$$\alpha_i = \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \quad (16)$$

$$m_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2 \quad (17)$$

For mixtures an appropriate mixing rule is employed as mentioned in the previous chapter. Above cubic equation expressed by the compressibility factor yields one or three roots (Z) depending upon the number of phases in the system. In the two-phase region, the largest root is for the compressibility factor (Z_V) of the vapor while the smallest positive root corresponds to that (Z_L) of the liquid.

The component fugacity coefficients are calculated from an EOS that is reformulated in terms of the mixture description and is applicable to both the vapor and liquid phases. The calculation of $\phi_{L,i}$ is based on the liquid phase composition and when solving the EOS for the density or specific volume, the intermediate and vapor phase roots are discarded. Similarly, only the vapor phase root is required when calculating $\phi_{V,i}$ and the vapor phase composition is employed in its calculation. The liquid phase component fugacity coefficients ($\phi_{L,i}$) are calculated from the relation as below:

$$\ln \phi_{L,i} = \frac{b_i}{b} (Z_L - 1) - \ln(Z_L - B) - \frac{A}{B} \left(\frac{2}{a} \sum_j x_j a_{ij} - \frac{b_i}{b} \right) \ln \left(1 + \frac{B}{Z_L} \right) \quad (18)$$

where Z_L is the liquid root of the above compressibility expression. The identical equation is written for the vapor phase fugacity coefficient ($\phi_{V,i}$).

3. Peng-Robinson (PR) EOS Model

Peng and Robinson [1976] took note of the frequent failure of the SRK EOS to generate satisfactory liquid densities and presented a new EOS which was somewhat improved in this regard. They proposed an equation of the form as follows:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (19)$$

The compressibility factor (Z) expression of the PR EOS can be derived as follows:

$$Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0 \quad (20)$$

$$\text{with } A = \frac{a_i P}{R^2 T^2} \text{ and } B = \frac{b_i P}{RT} \quad (21)$$

For single components a_i and b_i are obtained from:

$$a_i = a_i \alpha_i \quad (22)$$

$$\text{where } \alpha_i = 0.45724 \frac{R^2 T_{c,i}^2}{P_{c,i}} \quad (23)$$

$$\alpha_i = \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \quad (24)$$

$$m_i = 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2 \quad (25)$$

$$b_i = 0.07780 \frac{RT_{c,i}}{P_{c,i}} \quad (26)$$

The component fugacity coefficients ($\phi_{i,L}$) for the liquid phase are calculated from the bellows and the vapor phase fugacity coefficients ($\phi_{i,V}$) are calculated from the identical equation:

$$\ln \phi_{i,L} = \frac{b_i}{b} (Z_L - 1) - \ln(Z_L - B) - \frac{A}{2\sqrt{2}B} \left[\frac{2}{a} \sum_j x_j a_{ij} - \frac{b_i}{b} \right] \ln \left[\frac{Z_L + (1 + \sqrt{2})B}{Z_L + (1 - \sqrt{2})B} \right] \quad (27)$$

4. Component Lumping Procedure

The type of lumping which has commonly been used is "pseudocomponent lumping" in which the mixture components are divided into component classes called pseudocomponents. The vapor-liquid equilibrium calculations are performed with these pseudocomponents as if they were real, physical components. The analytical lumping technique developed by Whitson [1983] was used to approximate a crude oil as several discrete classes. Since a large number of compounds are grouped into these pseudocomponents, there are inherent uncertainties in the lumping process. An alternative to component lumping is "continuous thermodynamics" where the mixture is represented by a continuous distribution rather than discrete pseudocomponents [Kehlen et al., 1985; Rätzsch et al., 1988]. Equilibrium criteria must be reformulated to perform the vapor-liquid equilibrium calculation for both discrete lumping and continuous distribution techniques. Pseudocomponent lumping has proven to be a most effective method in the representation of crude oils for phase equilibrium calculations [Whitson, 1983; Riazi and Daubert, 1987]. Pseudocomponent lumping was chosen as the initial techniques to model the extraction process employed in this study.

The 35-components (petroleum fractions) crude oil system determined by the SIMDIS was lumped to 6 pseudocomponents (N_H) according to Whitson's lumping procedure as follows:

$$N_H = 1 + 3.3 \log(N - 7) \quad (28)$$

where N is the carbon number of the heaviest fraction in the original crude oil. The highest molecular weight normal paraffin identified in the SIMDIS chromatogram was C_{40} . Thus, carbon number 40 was assumed to be representative of the heaviest fraction of the crude oil and then N_H was computed to be 6. The groups were classified according to molecular weight (M_i) as determined from the SIMDIS analysis of the crude oil:

$$M_i = M_7 \left(\frac{M_N}{M_7} \right)^{1/N_H} \text{ where } i = 1, 2, \dots, N_H. \quad (29)$$

Since the concentrations of C_5 and C_6 hydrocarbons in this oil were very small, these components were lumped with the first C_7 -plus fraction.

EXPERIMENTAL

A schematic of the experimental system used in this study is presented in Fig. 1. The supercritical fluid extraction (SFE) system consists of three sections: the supercritical fluid supply system, the extractor assembly, and the separator assembly. A temperature controlled, 300 cc extractor was the central element of the system. The extraction vessel was an Autoclave Engineers, Inc.'s bolted-closure autoclave equipped with a magnetic-drive packerless stirring device. The mixing device was a turbine-type agitator provided with a hollow shaft used in conjunction with removable baffles in the vessel. High speed agitation at rates up

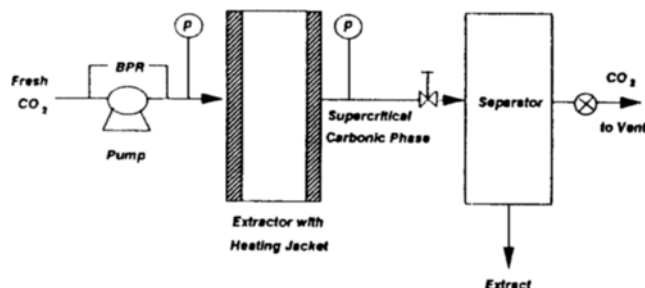


Fig. 1. Schematic of the supercritical fluid extraction system.

to 2500 rpm was achieved by the rotation of external magnets which actuated internal magnets fastened to the stirrer shaft. The inside diameter of the extraction vessel was 4.6 cm, thus the distance between the blade tip and the extractor wall was 0.6 cm. In operation, a low pressure area was created at the turbine impeller. The inlet CO_2 was drawn down through the hollow shaft and was dispersed through a crude oil feedstock. This type of agitation insured constant circulation and well mixing of supercritical CO_2 through the crude oil, which also led to ascertain the attainment of phase separation during a continuous extraction.

Initial charge of a hexadecane and crude oil used as a feedstock was 77 and 80 grams respectively, and the extracted samples during a process were collected in each about 20 minutes extraction time sequence corresponding to about 25 liters of CO_2 passed through the separator system. Experimental results in this extraction system were reproducible to within 2% experimental variability. Total mass recovery in excess of 95% was obtained in all the experiments. This extraction process was operated at thermodynamic equilibrium and the phase compositions of the extracted phases were analyzed using a simulated distillation (SIMDIS) and a gas chromatography-mass spectrometry (GC-MS). The properties of carbon number fractions of the crude oil used as a feedstock in the experiments were determined by the SIMDIS and a gel permeation chromatography (GPC), and is compared with those of normal alkane hydrocarbons (C_nH_{2n+2}) at Table 1. Specific gravities of each carbon number fraction were adopted from Katz and Firoozabadi [1978]'s generated properties. The characterized properties shown in Table 1 were used to perform the component lumping of crude oil and phase behavior calculations.

RESULTS AND DISCUSSION

1. Preliminary Process Test with Hexadecane and CO_2

Before crude oil extractions with supercritical CO_2 , the SFE system was preliminarily tested using hexadecane ($C_{16}H_{34}$) as a feedstock. The primary objective of the experiment was to ascertain the attainment of thermodynamic equilibrium during continuous extraction. This test was also performed to determine how various components of the SFE system functioned and to establish appropriate experimental procedures. Extractions were conducted at constant $38^\circ C$ and at two pressures: 10.3 MPa and 17.2 MPa. It is observed in Fig. 2 that a higher extraction yield of 68 wt% was obtained at the higher pressure of 17.2 MPa, and that the extraction yields increased linearly with extraction time.

Experiments with binary mixtures of hexadecane and CO_2 provided a simple system to test whether the fluids within the extractor are well mixed and existed in equilibrium. According to the phase rule, the phase compositions in the two-component, two-

Table 1. Properties of crude oil fractions used for lumping study

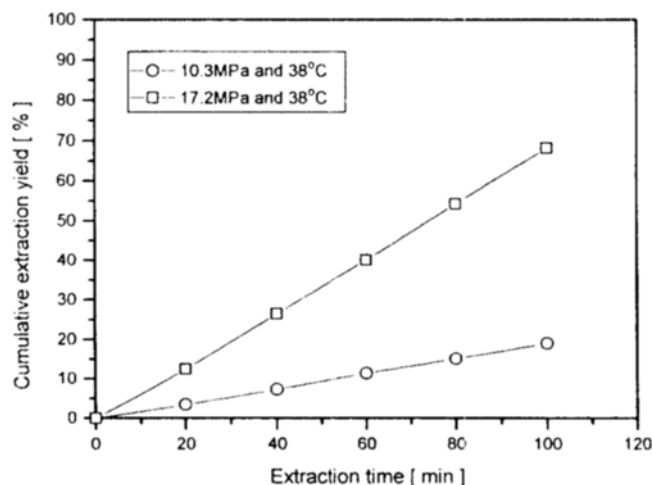
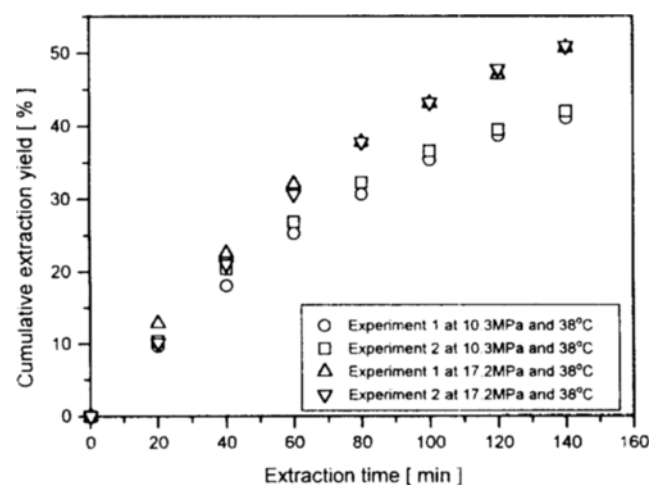
Crude oil fractions	Mol %	S.G. ^a	B.P.(°C)		M.W.	
			Crude ^b	n-Alkane ^c	Crude ^b	n-Alkane ^c
C ₅	0.1	0.631	34	36	72	72
C ₆	0.3	0.686	64	69	84	86
C ₇	3.0	0.724	92	98	96	100
C ₈	8.0	0.747	117	126	107	114
C ₉	6.9	0.766	142	151	121	128
C ₁₀	6.0	0.780	166	174	134	142
C ₁₁	5.0	0.791	187	195	147	156
C ₁₂	4.6	0.802	208	216	161	170
C ₁₃	4.1	0.813	227	235	175	184
C ₁₄	5.0	0.824	247	253	190	198
C ₁₅	5.2	0.834	266	270	206	212
C ₁₆	4.8	0.841	283	287	222	226
C ₁₇	5.6	0.849	300	302	237	240
C ₁₈	3.7	0.854	313	317	251	254
C ₁₉	3.2	0.859	325	331	263	268
C ₂₀	3.7	0.864	338	344	275	282
C ₂₁	2.8	0.869	351	357	291	296
C ₂₂	3.5	0.874	357	369	305	310
C ₂₃	3.0	0.879	375	380	318	324
C ₂₄	2.8	0.883	386	391	331	338
C ₂₅	3.0	0.887	397	402	345	352
C ₂₆	2.6	0.891	408	412	359	366
C ₂₇	2.6	0.895	418	422	374	380
C ₂₈	2.3	0.898	428	432	388	394
C ₂₉	1.9	0.901	436	441	402	408
C ₃₀	1.3	0.904	446	450	416	422
C ₃₁	1.1	0.908	456	459	430	436
C ₃₂	0.9	0.911	463	468	444	450
C ₃₃	0.7	0.914	472	476	458	464
C ₃₄	0.4	0.916	479	483	472	478
C ₃₅	0.4	0.919	487	491	486	492
C ₃₆	0.4	0.921	494	498	500	506
C ₃₇	0.3	0.924	501	505	514	520
C ₃₈	0.3	0.926	508	512	528	534
C ₃₉	0.3	0.928	515	518	542	548
C ₄₀	0.2	0.930	522	525	556	562

^aspecific gravity from Katz and Firoozabadi [1978]'s generalized properties

^bcharacterized properties of C₃₀ crude oil group.

^cproperties assumed by n-alkane (C_nH_{2n+2}).

phase system are fixed and invariant with respect to the overall system composition. As CO₂ was continuously introduced into the extractor in this study, the overall system became richer in CO₂. However, the phase compositions did not change. This should result in the production of the same amount of hexadecane as a function of time as the supercritical (carbonic-rich) phase is moved into the separator. The carbonic (extract) phase compositions at 10.3 MPa and 38°C were predicted from the equilibrium calculation using Peng-Robinson EOS, and the constancy of results (98.5 mol% of CO₂ and 1.5 mol% of hexadecane) was consistent with the experimental values that were 98.8 mol% of CO₂ and 1.2 mol% of hexadecane regardless of the extraction time proceeded. It was verified from the reasonable agreement between the calculation and experiment that the SFE studies reported here were carried out under conditions of thermodynamic equilibrium.

**Fig. 2. Extraction yield (%) for hexadecane (C₁₆H₃₄)-CO₂ system.****Fig. 3. Extraction yield (%) and experimental reproducibility for crude oil-CO₂ system.**

2. Crude Oil Extraction with CO₂

Extractions of crude oil with CO₂ were performed at constant 38°C and at two different pressures, 10.3 MPa and 17.2 MPa. Two experiments at identical conditions were conducted to assess the reproducibility of experimental data, and the results of extractions are presented in Fig. 3. In general, the amount of the extracted phases decreased as a function of extraction time and the most of extraction performance was reproducible to within 2% experimental variability. At higher pressure of 17.2 MPa, a higher extraction yield of 51 wt% was achieved. Extraction yields were governed by the density of CO₂ used as a solvent at the extraction conditions. The densities of pure CO₂ at 10.3 MPa and 17.2 MPa at 38°C are 0.6672 and 0.8254 g/cm³, respectively [Reid et al., 1977]. The amount extracted by the liquid carbonic phase increased with an increase in pressure and was related to the CO₂ density increase. The rates of extraction (the amount extracted per unit volume of CO₂) were also greater at higher pressure.

Compositional changes in the extracted phases which occurred during a SFE at 10.3 MPa and 38°C were monitored in an attempt to establish the nature of the extraction and partitioning process as a function of time. The carbon number distributions of the

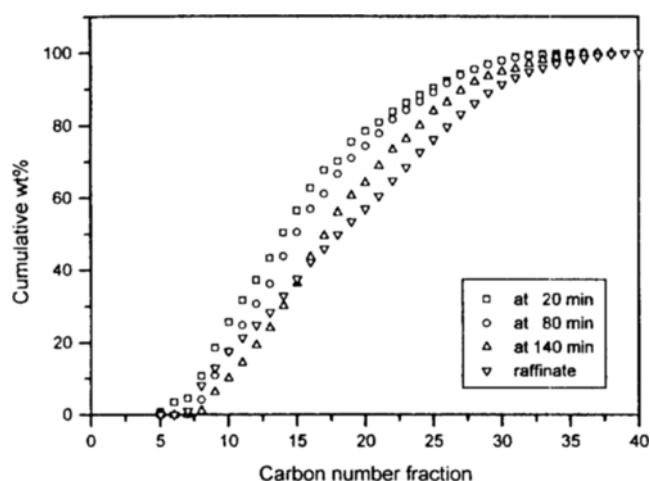


Fig. 4. Carbon number distribution of extracts and raffinate at 10.3 MPa and 38°C as a function of time for crude oil-CO₂ system.

Table 2. Characterization and pseudo-thermodynamic properties of pseudo-components used in the representation of a crude oil

	Pseudocomponents ^a					
	1	2	3	4	5	6
Content (wt%)	24.3	5.0	4.6	4.1	20.6	41.4
Specific gravity at 15°C	0.754	0.791	0.802	0.813	0.837	0.881
Boiling point (T _b , °C)	129	187	208	227	273	384
Pseudo-properties ^b						
P _c (MPa)	2.8	2.3	2.2	2.0	1.8	1.2
V _c (l/gmol)	0.45	0.57	0.63	0.67	0.84	1.15
T _c (°C)	310	369	390	408	451	568
Molecular weight (g/gmol)	114	147	161	175	213	338
Acentric factor	0.36	0.45	0.49	0.53	0.62	0.95
δ _{SRK} ^c	0.110	0.105	0.105	0.100	0.090	0.075
δ _{PR} ^d	0.113	0.110	0.105	0.100	0.100	0.070

^agrouped by Whiston [1983]'s lumping method.

^bestimated by a mole-average mixing rule and Kesler-Lee [1976] correlations.

^cinteraction parameter for SRK EOS model.

^dinteraction parameter for PR EOS model.

oils extracted as a function of time were obtained by the SIMDIS analysis and are presented in Fig. 4. It was clearly observed that the earlier extracts contain relatively lighter compounds, and that the carbon number distribution of the extract has shifted toward a heavier carbon number as the extraction proceeded. The color differences of the extracted samples also provided visual evidence of compositional variations as a function of time. The colors of the extracts at earlier times were relatively darker despite the lighter components extracted during this period. This fact may be explained by GC-MS analysis, which indicated that the relatively lesser amounts of paraffinic compounds and greater amounts of naphthenic and aromatic compounds were extracted at earlier extraction times.

3. Modeling of Extraction Process

A successful representation of above extraction of crude oil

Table 3. Extract phase compositions predicted by phase equilibrium calculations for crude oil-CO₂ system at 10.3 MPa and 38°C (unit in mol%)

Time (min)	EOS ^a	CO ₂	F ₁ ^b	F ₂ ^c	F ₃ ^d	F ₄ ^e	F ₅ ^f	F ₆ ^g
20	PR	96.05	2.35	0.28	0.23	0.17	0.52	0.40
	SRK	95.72	2.20	0.31	0.28	0.18	0.76	0.55
40	PR	96.48	2.03	0.25	0.21	0.15	0.49	0.39
	SRK	96.27	1.85	0.28	0.25	0.16	0.70	0.49
60	PR	96.85	1.75	0.23	0.19	0.14	0.47	0.38
	SRK	96.77	1.58	0.24	0.22	0.14	0.65	0.40
80	PR	97.17	1.51	0.21	0.17	0.13	0.44	0.37
	SRK	97.14	1.39	0.22	0.20	0.13	0.59	0.33
100	PR	97.39	1.34	0.20	0.16	0.12	0.43	0.36
	SRK	97.44	1.20	0.20	0.18	0.11	0.56	0.31
120	PR	97.61	1.18	0.18	0.15	0.12	0.41	0.35
	SRK	97.72	1.05	0.17	0.15	0.10	0.52	0.29
140	PR	97.74	1.09	0.17	0.14	0.11	0.40	0.35
	SRK	98.02	0.88	0.14	0.13	0.08	0.48	0.27

^aequation of state used in phase equilibrium calculations.

^bF₁: pseudocomponent 1 which represents C₅-C₁₀ fraction of extracted oil.

^cF₂: pseudocomponent 2 which represents C₁₁ fraction of extracted oil.

^dF₃: pseudocomponent 3 which represents C₁₂ fraction of extracted oil.

^eF₄: pseudocomponent 4 which represents C₁₃ fraction of extracted oil.

^fF₅: pseudocomponent 5 which represents C₁₄-C₁₇ fraction of extracted oil.

^gF₆: pseudocomponent 6 which represents C₁₈-C₄₀ fraction of extracted oil.

mixtures with CO₂ requires the specification of an appropriate equation of state, the development of a pseudocomponent lumping scheme, and the calculation of pseudocritical properties to represent the extraction process. The SRK and PR EOSs were used for the vapor-liquid equilibrium calculations and to predict the compositions of the extract phase which is the supercritical carbonic phase [Ngheim et al., 1983]. The 36 fractions of the crude oil generated by the SIMDIS analyses as shown in Table 1 were lumped into six pseudocomponents using a Whiston [1983]'s lumping procedure as mentioned in the previous introduction chapter. Once the six pseudocomponents were chosen, the critical properties (T_c, P_c, V_c), the molecular weight, the acentric factor, and the interaction parameters of these pseudocomponents were calculated from the specific gravity and the mean average boiling point which were assigned from the Table 1. A simple mole-average mixing rule and Kesler-Lee [1976] correlations were used in these calculations. The similar trend of interaction parameters (δ_{ij}) proposed by Nutakki [1989], which are decreased with the carbon number of the normal alkanes, was obtained between CO₂ and the pseudocomponents in this estimation. These interaction parameters were adjusted with the non-linear regression method until the most reasonable agreement was found between calculated and experimental results.

The extract phase compositions at 10.3 MPa and 38°C as a function of time were calculated using two different EOSs and are tabulated in Table 3. The predicted carbonic (extract or supercritical) phase compositions changed as a function of extraction time regardless of the type of EOS used. Compositional changes

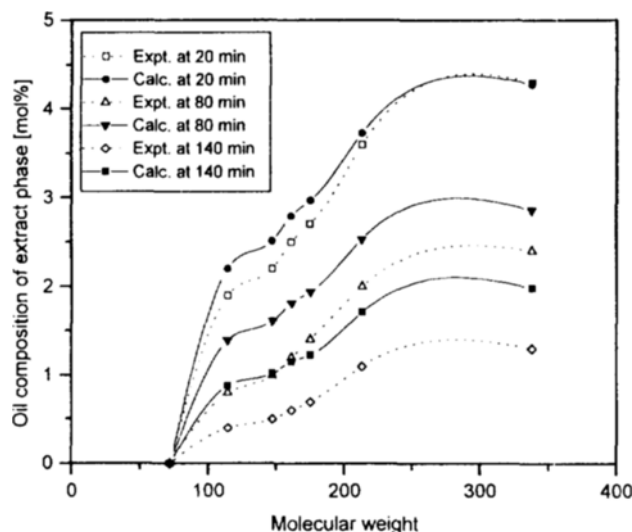


Fig. 5. Molecular weight distribution of oil compositions existed in the extract phase using Soave-Redlich-Kwong equation of state for crude oil-CO₂ system at 10.3 MPa and 38°C.

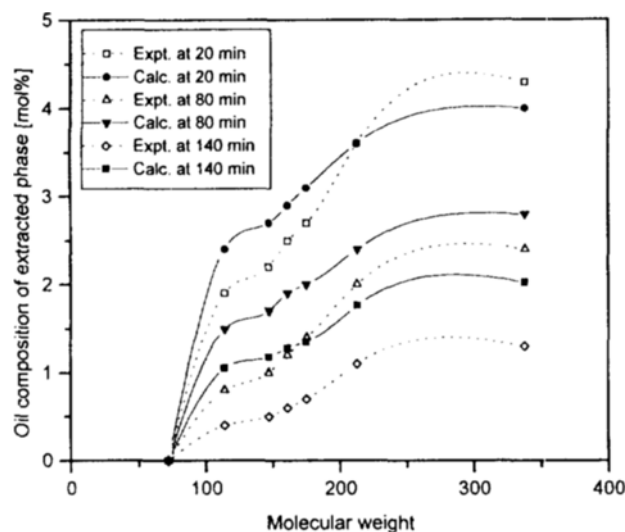


Fig. 6. Molecular weight distribution of oil compositions existed in the extract phase using Peng-Robinson equation of state for crude oil-CO₂ system at 10.3 MPa and 38°C.

in the extracted phases which occurred during SFE were clearly predicted in these modeling results, which established the nature of the extraction and partitioning process as a function of time. The molecular weight distributions of 6 pseudocomponents of the oil existed in the extract phase were also obtained from the equilibrium calculations using two different EOSs and then are compared with the experimental data determined by the SIMDIS analysis at Figs. 5 and 6. It was observed from the modeling results as seen from the earlier experimental results that the earlier extracts contain relatively lighter compounds, and that the molecular weight distribution of the extract has shifted toward a heavier molecular weight number as the extraction proceeded. For the longer extraction time corresponding to the heavier fractions extracted, the larger differences between the experimental and calculated values were observed from both EOS models. Slightly

better agreement between the experimental and calculated values was shown in the results of SRK EOS model, which is modified from the Redlich-Kwong EOS to force a fit to saturation pressures of pure nonpolar and slightly polar substances, rather than those of PR EOS model. General agreement between the experimental and calculated values as shown in Figs. 5 and 6 was reasonable considering the uncertainties involved in modeling such a complex process regardless of the type of EOS used.

In fact, when investigating the phase-behavior calculations for higher pressure of 17.2 MPa, it was discovered that the model predicted a phase-flip for a certain set of overall compositions even though this phase-flip phenomenon was not observed experimentally. The volume translation concept would be contributed to correct the errors caused by this phase-flip in the phase density calculations [Nutakki, 1989; Sheng and Lu, 1990]. This and the rest of the modeling uncertainties addressed in this study would be overcome and explained by a more comprehensive modeling study including the followings: (1) more accurate technique (i.e. other lumping schemes, continuous thermodynamics, etc.) to represent the complex hydrocarbon mixtures such as a crude oil; (2) better prediction of thermodynamic properties (i.e. critical properties, acentric factor, interaction parameter, etc.) of heavy pseudo-components fractions resulting in the large differences between the experimental and calculated values. (3) the appropriate choice of the equation of state and mixing rule with regard to the chemical nature (i.e. polarity, volatility, etc.) of the CO₂ and crude oil mixtures in predicting the phase-equilibrium compositions; and (4) the appropriate time interval over which the flash calculations ought to be performed for accurate representation of the extraction performance.

CONCLUSIONS

Continuous multiple-contact extractions of a hexadecane and crude oil by supercritical CO₂ were successfully carried out to understand the nature of the extraction and partitioning process as a function of pressure and extraction time. Extraction yields were governed by the density of CO₂ and increased with pressure increase. The rates of extraction (the amount extracted per unit volume of CO₂) were also greater at higher pressure. Heavier compounds were extracted as extraction time. Color differences between extracted samples also provided visual evidence of compositional variations.

Two different EOSs and a lumping method were successfully used to model the extraction performance of complex hydrocarbon mixtures with supercritical CO₂ as a function of time. The continuously changing compositions in the extract phase were also predicted from the phase equilibrium calculations using the SRK and PR EOSs and then are compared with the experimental data obtained during SFE. The agreement between the experimental data and the calculated values was reasonable considering the uncertainties in modeling such a complex hydrocarbon system.

NOMENCLATURE

- $f_{L,i}$: fugacity coefficient of component i of liquid phase
- $f_{V,i}$: fugacity coefficient of component i of vapor phase
- K_i : equilibrium constant of component i
- M_l : molecular weight of lumped group of l

M_N : molecular weight of petroleum fraction of last carbon number
 M_7 : molecular weight of petroleum fraction of carbon number 7
 $m.w.$: molecular weight [g/gmol]
 N_H : number of hypothetical groups
 P_c : critical pressure [MPa]
 $s.g.$: specific gravity at 15°C
 T_b : boiling point [°C]
 T_c : critical temperature [°C]
 V_c : critical volume [1/gmol]
 x_i : liquid mole fraction of component i
 y_i : vapor mole fraction of component i
 Z : compressibility factor
 Z_L : liquid root of compressibility factor equation with cubic form

Abbreviations

BPR : back pressure regulator
 Calc. : calculated value
 EOR : enhanced oil recovery
 EOS : equation of state
 Expt. : experimental data
 GC-MS : gas chromatography-mass spectrometry
 GPC : gel permeation chromatography
 PR : Peng-Robinson
 SFE : supercritical fluid extraction
 SIMDIS : simulated distillation
 SRK : Soave-Redlich-Kwong
 SS : successive substitution

Greek Letters

ω_i : acentric factor of component i
 δ_{ij} : interaction parameter between components i and j
 $\phi_{L,i}$: fugacity coefficient of component i of liquid phase
 $\phi_{V,i}$: fugacity coefficient of component i of vapor phase

Subscripts

i : component i
 j : component j
 ij : components i and j
 L,i : component i of liquid phase
 V,i : component i of vapor phase

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