Lawrence Berkeley National Laboratory

Recent Work

Title

SUPERCRITICAL-FLUID EXTRACTION CALCULATIONS FOR HIGH-BOILING PETROLEUM FRACTIONS USING PROPANE. APPLICATION OF CONTINUOUS THERMODYNAMICS

Permalink <https://escholarship.org/uc/item/9vp3w9f7>

Authors

Cotterman, R.L. Dimitrelis, D. Prausnitz, J.M.

Publication Date

1984-04-01

 ϵ .

 $-36 - 179$

UNIVERSITY OF CALIFORNIA **RESERVIAL RUNDERSITY OF CALIFORNIA**

Materials & Molecular Research Division

JUN 12 1984

LIBRARY AND DOCUMENTS SECTION

Presented at the Discussion Meeting of the Deutsche Bunsen-Gesellschaft fuer Physikalische Chemie, Koenigstein, W. Germany, April 4-6, 1984; and to be published in the Proceedings

SUPERCRITICAL-FLUID EXTRACTION CALCULATIONS FOR HIGH-BOILING PETROLEUM FRACTIONS USING PROPANE. APPLICATION OF CONTINUOUS THERMODYNAMICS

R.L. Cotterman, D. Dimitrelis, and J.M. Prausnitz

April 1984

 $\sum_{i=1}^{n}$

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

SUPERCRITICAL-FLUID EXTRACTION CALCULATIONS

FOR HIGH-BOILING PETROLEUM FRACTIONS USING PROPANE.

APPLICATION OF CONTINUOUS THERMODYNAMICS

Ronald L. Cotterman, Dimitrios Dimitrelis and John M. Prausnitz

Materials and Molecular Research Division

Lawrence Berkeley Laboratory

and

Department of Chemical Engineering University of California, Berkeley, CA 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

...

ABSTRACT

Supercrltical-fluid extraction is a useful process for upgrading heavy multicomponent mixtures such as high-boiling petroleum fractions. Designoriented calculations are reported for an extraction process using propane to extract intermediate components from a petroleum fraction with molecular weights in the range 150-500.

..

The composition of the heavy-hydrocarbon mixture is described by two continuous distribution functions of molecular weight, one for paraffinic and one for aromatic components. Process calculations are based on a recently developed thermodynamic framework for mixtures with very many components, coupled with an equation of state of the van der Waals form.

Particular attention is given to multicomponent phase equilibria in the retrograde region where solvent recovery is favorable. Quantitative results are given for solvent capacity and selectivity as a function of operating conditions.

1. Introduction

.•

...

Supercritical-fluid extraction is a useful process for upgrading heavy crude petroleum residua, for extracting polymer blends or for purifying natural products such as vegetable oils $\{1,2,3,4\}$. A common characteristic of these systems is that they are mixtures with very many components. While the study of binary or ternary mixtures [5,6,7] is important for understanding the effects of process variables on supercritical-fluid extraction of desired products, for engineering design it is often necessary to describe the properties of mixtures with very many components.

Figure 1 shows a schematic of a supercritical extraction process (e.g. propane deasphalting). A heavy crude residuum is to be upgraded using a supercritical solvent. In a typical extractor, supercritical propane may extract from the crude the lighter components; it is then separated from the solutes in a second step by temperature increase or pressure drop and finally, it is recycled back to the extractor. Efficient solvent regeneration *is* the most important advantage when supercritical-fluid extraction is compared with conventional liquid-liquid extraction.

In this work we discuss application to supercritical-fluid extraction of recent work [8,9] on the framework of continuous thermodynamics (i.e. thermodynamics of mixtures with very many components). Continuous thermodynamics provides a useful method for calculating phase equilibria for those mixtures where conventional quantitative chemical analysis is not available but where the mixture's composition is given by some statistical description. We present illustrative calculations to indicate the effect of operating conditions (temperature T and pressure P) on supercritical extraction of a continuous mixture consisting of two ensembles (paraffins and aromatics). We

 $-1-$

also discuss conditions leading to preferential extraction of lighter hydrocarbons and selective extraction of paraffins relative to aromatics.

2. Procedure

2.1 Thermodynamic Framework

Figure 2 contrasts the compositions of a discrete and a continuous mixture. On the left, the composition of a mixture with a finite number of components (in this case ten) is characterized by mole fractions x_i (for each component i) indicated by a bar; the sum of all mole fractions equals unity. For a continuous mixture (i.e. a mixture with very many components), shown on the right of Figure 2, we describe the composition of the mixture in terms of a distribution variable I (e.g. molecular weight); instead of mole fractions, we now have a distribution function $F(I)$ such that $F(I)$ ΔI is the fraction of moles within the range I to I+AI. The normalization condition is now given by an integral shown at the bottom.

Suppose that we have a liquid phase (L) and a supercritical phase (SF) at equilibrium; as discussed elsewhere [8], the conditions for equilibrium for the case of a semi-continuous mixture are

$$
T^L = T^{SF} \qquad (1)
$$

•'

,.

$$
P^L = P^{SF} \qquad (2)
$$

for every discrete component i

$$
f_{\mathbf{1}}^{\mathbf{L}} = f_{\mathbf{1}}^{\mathbf{SF}} \tag{3}
$$

and for every continuous component

$$
f^{L}(I) = f^{SF}(I) \quad \text{for all } I, \tag{4}
$$

where fugacity f can be calculated from an equation of state; for the fugacity of a continuous component in the liquid phase, we have

$$
\ln \frac{f^{L}(I)}{F^{L}(I) P} = \int_{V} \left(\frac{e^{(P/RT)}}{6(n_{T}^{L} F^{L}(I))} \right) T_{V} V_{V} I^{\dagger} - \frac{1}{V} dV - \ln \frac{P V^{L}}{n_{T}^{L} F^{L}(I) RT}
$$
(5)

where $\mathfrak{n}^{\rm L}_{\rm T}$ is the total number of moles of continuous component and ${\tt V}^{\rm L}$ is the volume of the liquid phase. Symbol δ stands for the functional derivative operator [8,10]. A similar relation holds for the fugacity in the supercritical phase.

Flash calculations are essential for engineering design of supercriticalextraction processes, as indicated in Figure 3. Given the temperature, pressure and feed composition, it is necessary to calculate compositions and relative amounts of the two outlet streams. The outlet streams are assumed to be in thermodynamic equilibrium; further, feed and outlet streams are related through material balances. Material balances and phase equilibria must be solved simultaneously using numerical methods as discussed elsewhere $[9]$.

2.2 Fluid-Phase Equilibria for a Semi-continuous Mixture of Propane with Heavy Hydrocarbons

For illustrative purposes, we represent the heavy crude residuum by a model mixture consisting of two ensembles, paraffins and aromatics. Figure 4 shows the assumed distributions that describe the feed. Throughout these calculations we assume that !n the feed the molar ratio of paraffins to aromatics is 3. We further assume that the molar distributions in the feed are given by a gamma distribution function [11] with mean molecular weights of 200 and 225, and variances of 1000 and 1600, respectively • The molecular weight of the lightest paraffin is 150 and that of the lightest aromatic is 170. However, our calculational procedure is not restricted by a particular choice of distribution function. The distribution could be specified in a functional form (as is

..

....

-3-

the case here) or by numerical data at selected points in a range of the characterizing quantity I.

To represent the phase behavior of the propane/heavy-hydrocarbon mixture, we use an equation of state similar to that of Redlich-Kwong as modified by Soave [12]. This choice restricts us in the upper limit of heavies to approximately !=500 (molecular weight). Pure-component equation-of-state parameters a and bare fitted to vapor-pressure data as a function of molecular weight (MW):

$$
b = b^{(0)} + b^{(1)} [MW]
$$
\n
$$
a^{1/2} = a^{(0)}(T) + a^{(1)}(T) [MW]
$$
\n(7)

for normal paraffins from C_4 to C_{40} and for alkylbenzenes from C_6 to C_{22} [9]. For the mixture we use conventional mixing rules as discussed elsewhere [8,9]. For binary interaction parameter a_{rs} , we use

I

$$
a_{rs} = (a_{r}a_{s})^{1/2}(1-k_{rs}). \tag{8}
$$

From experimental vapor-liquid equilibrium (VLE) data, we obtain for propaneparaffins,

$$
k_{rs} = -0.05 + 0.1264 \exp(-0.0068 \text{ [MW]}).
$$
 (9)

Because of the small number of VLE data available for propane-alkylbenzene binaries, k_{rs} is set equal to 0.03, independent of molecular weight. For the paraffins-aromatics interactions, we set k_{rs} equal to zero.

Figure 5 shows a pressure-temperature diagram for semi-continuous mixtures of propane with heavy hydrocarbons. Shown are the vapor pressure curve for pure propane and isopleths (lines of constant composition) for mixtures. From the locations of the calculated mixture critical points, we can conclude that there is a continuous critical locus between the critical point

of pure propane and the critical point of the 100 mole % heavies isopleth. This is consistent with experimental evidence that the first propane/n-alkane system which exhibits a discontinuous critical locus ls for a heavy component above C_{40} [13]; our system is a Type I mixture according to the classification of Scott and van Konynenburg [14] •

Our phase-diagram calculations are performed using a direct-substitution method, described elsewhere [15]. A one-dimensional Newton-Raphson iteration is used to converge for the fraction vaporized using the Rachford-Rice objective function [16]. Estimated K-factors are updated for each iteration by successive substitution. We define K-factors :

$$
K_{\underline{t}} = \frac{y_{\underline{t}}}{x_{\underline{t}}} \tag{10}
$$

for a discrete component i and

$$
K(I) = (\frac{n^{SF}}{n^{L}}) (\frac{F^{SF}(I)}{F^{L}(I)})
$$
 (11)

for a continuous component (see Figure 3).

This numerical procedure is stable; it converges smoothly and rapidly at low and moderate pressures. However, in the retrograde region, near the mixture critical point, good initial guesses of compositions are necessary and a large number of iterations are required for convergence. More efficient computational methods are now under development [17].

3. Results

. ..

Figure 6 shows the effect of pressure on the extraction of a mixture of heavy hydrocarbons at 520 K. The feed is composed of 90 mole % propane; the

-5-

remaining 10 mole % are heavies. Results are presented for 6 and 10 MPa in the form of molar distribution functions (defined as the number of moles of continuous component in a given stream within the range I to I+AI on the basis of 1 mole total feed) for both ensembles, paraffins and aromatics, in the feed (specified) and in the outlet (calculated) streams. Comparing peak heights in the extract phase for both ensembles, we see an increase with rising pressure. Raising the pressure from 6 to 10 MPa, therefore, increases solvent capacity which is here defined as the mole fraction of heavies (paraffins and aromatics) in the fluid phase.

While solvent capacity is an important design variable, more important is solvent selectivity. Of interest here are two types of selectivity. The first is with respect to molecular weight and the second is with respect to molecular structure (paraffins versus aromatics).

We can qualitatively understand the effect of pressure on the preferential extraction of intermediate hydrocarbons (paraffins or aromatics) by comparing the shape of the calculated distribution function for the fluid phase at one pressure with that of another pressure. As shown in Figure 6, at 6 MPa, the fluid-phase distribution function indicates that there is essentially no extraction for hydrocarbons with a molecular weight larger than (about) 280. However, at 10 MPa, the fluid-phase distribution function indicates that there is essentially no extraction for hydrocarbons with a molecular weight larger than (about) 320. These results suggest that, in the region investigated, selectivity (of the first kind) falls with rising pressure.

For more detailed quantitative calculations of capacity and selectivity, we consider a mixture where the molar solvent-to-feed ratio is $96/4$ (z =0.96). While this molar ratio is high, the corresponding mass ratio is much lower.

-6-

This ratio is representative of conditions in the second stage of a multi-stage extraction process [18]. For these conditions, the retrograde region is large, as shown in Figure 7.

Figure 8 shows that at constant pressure the capacity depends strongly on temperature. At pressures near 7 or 8 MPa, which are above the mixture critical point, capacity decreases drastically when the temperature is raised slightly. For the 7 MPa isobar, a change from 420 to 430 K decreases the capacity by a factor of two. As indicated in Figure 8, it is not desirable to operate at *5* MPa because a change in temperature will not be useful for solvent regeneration.

Figure 9 shows selectivity (of the second kind) as a function of temperature; at the conditions considered here, propane prefers paraffins (P) to aromatics (A). Selectivity $\beta p/A$ is defined by

$$
\beta_{P/A} = \frac{(n^{SF}/n^{L})_{Paraffins}}{(n^{SF}/n^{L})_{Aromatic}}
$$

,.,.

At 7 MPa, selectivity is highly sensitive to temperature. Therefore, if the purpose of the extraction is to remove paraffins from aromatics, it may be desirable to use a multistage process at 7 MPa where the temperature changes, from one stage to another, in the region 420 to 430 K.

Figure 10 presents K-factors (eq. 10) for paraffins and for aromatics as a function of molecular weight. Figure 10 shows that selectivity of the first kind is good at all these pressures but it is best at 5 MPa where the slope of the line is largest. At pressures above 8 MPa, the lines tend to flatten, giving poor selectivity of the first kind.

-7-

At *a* fixed molecular weight, the ratio of K-factors (paraffins/aromatics) gives the selectivity (of the second kind) as *a* function of molecular weight, shown in Figure 11. We see that the selectivity is low at lower molecular weights but rises with increasing molecular weight; further, selectivity is better at lower pressures.

The results shown in Figures 10 and 11 indicate that propane is a useful solvent if the purpose of the extraction is to obtain separation with respect to molecular weight; it is only moderately useful if the purpose of the extraction ls to obtain separation with respect to molecular structure.

The calculations presented here are for mixtures with molecular weights below 500. In present petroleum technology, primary interest in supercritical extraction ls directed at mixtures with considerably higher molecular weights. While the calculational procedures discussed here are not limited with respect to molecular weight, we have not presented results for very-high-molecularweight mixtures because, for our illustrative purposes, we used an equation of state of the Redlich-Kwong-Soave form; unfortunately, that equation of state is not suitable for hydrocarbons with molecular weights appreciably in excess of 500. However, calculations for such mixtures are possible when we use a perturbed-hard-chain equation of state; such calculations are now in progress.

Supercritical extraction is most useful in the retrograde region. When propane is the solvent, the size of this region increases with the molecular weight of the heavy hydrocarbons [19]. A large retrograde region is desirable because it permits flexibility in setting temperature and pressure for optimum operation.

-8-

4. Conclusions

"

..

The operational advantage of supercrltical-fluid extraction is efficient solvent recovery. Flash calculations using continuous thermodynamics provide detailed process information for both extract and raffinate streams at given operating conditions. We have illustrated the advantages of such calculations for extraction of a 3:1 paraffin/aromatic mixture with supercrltical propane.

Using a modified Redlich-Kwong-Soave equation of state, we found that, in the retrograde region, rising pressure decreases preferential extraction of paraffins to aromatics but increases the capacity of the heavies in the supercritical-fluid phase. For paraffin-aromatic residua, propane is a good selective solvent with respect to molecular weight but only a modest one with respect to molecular structure.

The results presented for solvent capacity and paraffin/aromatic selectivity depend, in general, on the values of binary parameter k_{res} . We found that for propane/heavy hydrocarbons, the results are relatively insensitive to reasonable values of k_{res} . However, for other solvents (e.g. carbon dioxide), results are often sensitive to the binary parameters. In some cases, these binary- parameters may affect the qualitative shape of the phase diagram (change from type I to type III) [20].

While the illustrative calculations presented in this paper are for relatively simple mixtures, the procedure can be applied to any mixture for which we can establish a suitable molecular-thermodynamic equation of state. The important conclusion of our work is that we can now make realistic calculations for supercritical extraction of mixtures containing very many components as encountered in industrial practice.

-9-

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03~76SF00098. For partial financial support, the authors are also grateful to the Fannie and John Hertz Foundation, to Exxon Research and Engineering Company, to the Donors of the Petroleum Research Fund, administered by the American Chemical Society and to the National Science Foundation.

References

 $-$

- [1] M.E. Paulaitis, V.J. Krukonls, R.T. Kurnik and R.C. Reid, Rev. Chern. Eng. 1, 179 (1983).
- [2] D.F. Williams, Chern. Eng. Sci. 36, 1769 (1981).
- [3] N. Gangoli and G. Thodos, IEC Prod. Res. Dev. 16, 208 (1977).
- [4] G.M. Schneider, E. Stahl and G. Wilke (Eds.), "Extraction with Supercritical Gases", Verlag Chemie, Weinheim, West Germany, 1980.
- [5] R.T. Kurnik and R.C. Reid, Fluid Phase Equilibria 8, 93 (1982).
- [6] K.P. Johnston and C.A. Eckert, AIChE J. 27, 773 (1981).
- [7] R.J. Topliss, D. Dimitrelis and J.M. Prausnitz, LBL-Report 15065, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, USA, 1982.
- [8] R.L. Cotterman, R. Bender and J.M. Prausnitz, IEC Proc. Des. Dev. (1984) (in press).
- [9] R.L. Cotterman and J.M. Prausnitz, IEC Proc. Des. Dev. (1985) (submitted for publication).
- [10] J.P. Hansen and I.R. McDonald, "Theory of Simple Liquids", Academic Press, New York, NY, USA, 1976.
- [11] N.L. Johnson and S. Kotz, "Continuous Univariate Distributions-!", Houghton Miffin Company, Boston, MA, USA, 1970.
- [12] G. Soave, Chem. Eng. Sci. 27, 1197 (1972).
- [13] J.S. Rowlinson and F.L. Swinton, "Liquids and Liquid Mixtures", Butterworths, London, England, 1982, 3rd ed.
- [14] R.L. Scott and P.H. van Konynenburg, Discuss. Faraday Soc. 49, 87 (1970).
- [15] J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. 0 'Connell, "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria", Prentice Hall, Englewood Cliffs, NJ, USA, 1980.
- [16] H.H. Rachford and J.D. Rice, J. Pet. Tech., 4, 10, sec. 1, 19, sec. 2, 3, (1952).
- [17] R.J. Topliss, Dissertation, University of California, Berkeley, CA, USA, 1984.
- [18] J.A. Gearhart and S.R. Nelson, "ROSE®-Process Offers Energy Savings for Solvent Extraction", Paper presented at the 5th Annual Industrial Energy Conservation Technology Conference and Exhibition, Houston, TX, USA, 1983.
- [19] M.R. Brule and R.W. Corbett, "Modeling Critical~Solvent Processes", Paper presented at the AIChE Diamond Jubilee Meeting, Washington, DC, USA, 1983&
- [20] R.L. Cotterman, D. Dimitrelis and J.M. Prausnitz, Work in Progress.

List of Figure Captions

- Figure 1: Supercritical Fluid Extraction Calculations for High-Boiling Petro leum Fractions Using Propane.
- Figure 2: Discrete and Continuous Composition for a Multicomponent Mixture.
- Figure 3: Flash Calculation for a Semi-Continuous Mixture.
- Figure 4: Molar Distribution of Heavies in the Feed (z =0.9; $n_{\text{Paraffins}}^{\text{F}} = 0.075$; $n_{\text{Aromatics}}^{\text{F}}$ =0.025)
- Figure 5: Pressure-Temperature Diagram for a Semi-continuous Mixture of Propane with Paraffins and Aromatics (Paraffins/Aromatics=3).
- Figure 6: Effect of Pressure on the Extraction of a Continuous Mixture Contalning Paraffins and Aromatics Using Propane as a Solvent $(T = 520 K;$ $z_{C_3H_8} = 0.9$.
- Figure 7: Pressure-Temperature Diagram for a Semi-continuous Mixture of Propane with Heavy Hydrocarbons (z = 0.96; n_F^F = 0.03; n_F^F = 0.01).
C₃H₈ Paraffins Aromatics
- Figure 8: Effect of Temperature on Solvent Capacity at Constant Pressure $(z_{C₃H₈} = 0.96)$
- Figure 9: Effect of Temperature on Paraffin/Aromatic Selectivity at Constant Pressure $(z_{\alpha,n} = 0.96)$. c_3 _H $_8$
- Figure 10: K-Factors for the Continuous Fractions in the Propane/Heavy-Hydrocarbon System (T = 450 K; $z_{C_3H_8}$ = 0.96)

Figure 11: Paraffins/Aromatics Selectivity in the Propane/Heavy-Hydrocarbon

System (T = 450 K; $z_{C_3H_8}$ = 0.96).

SUPERCRITICAL FLUID EXTRACTION CALCULATIONS FOR HIGH-BOILING PETROLEUM FRACTIONS USING PROPANE

The solvent is supercritical to facilitate solvent recovery

Figure 1

DISCRETE AND CONTINUOUS COMPOSITION FOR A MULTICOMPONENT MIXTURE

-16-

I is a characterizing quantity, e.g., molecular weight.

FLASH CALCULATION FOR A SEMI-CONTINUOUS MIXTURE

 $-17-$

Must satisfy:

Phase Equilibria $f_i^{SF} = f_i^L$ $f^{SF}(I) = f^L(I)$ for all I

SF= supercritical fluid $L =$ liquid

Material Balance

 $z_i = \xi y_i + (1 - \xi) x_i$ $\eta^F F^F(I) = \xi \eta^{SF} F^{SF}(I) + (I-\xi) \eta^L F^{L}(I)$

- $\boldsymbol{\xi}$ fraction of feed in extract
- mole fraction of the continuous component $\boldsymbol{\eta}$

MOLAR DISTRIBUTION OF HEAVIES IN THE FEED

 $-18-$

$$
\left(\frac{\text{poraffins}}{\text{aromatics}}=3\right)
$$

 $-19-$

Figure 5

EFFECT OF PRESSURE ON THE EXTRACTION OF A CONTINUOUS MIXTURE CONTAINING PARAFFINS AND AROMATICS USING

PROPANE AS A SOLVENT $(T = 520K; z_{C3}H₈ = 0.90)$

Figure 6

PRESSURE-TEMPERATURE DIAGRAM FOR A SEMI-CONTINUOUS MIXTURE OF PROPANE WITH HEAVY HYDROCARBONS

 $(z_{C-H} = 0.96)$ $3^{\square}8$

-21-

Figure 9

K-FACTORS OF THE CONTINUOUS FRACTIONS IN THE PROPANE/HEAVY-HYDROCARBON SYSTEM $(T = 450 \text{ K}; z_{CH} = 0.96)$ $3^{11}8$ $10⁻¹$ $P = 8 MPa$ " " " $\overline{7}$ K - factor 10^{-2} " 7 " " " " " -- Paraffins " ".. ⁵ **Aromatics** " " " 10^{-3} \
200 250 300 350 150 Molecular Weight

Figure 10

 $-24-$

Figure 11

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

•

..

. ..,

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

بعدات

TECHNICAL INFORMATION DEPARTMENT LAWRENCE BERKELEY LABORATORY UNIVERSITY OF CALIFORNIA BERKELEY, CALIFORNIA 94720