

# Optimizing Supercritical Fluid Extraction Systems

Greg Rampley and Warren Stiver\*

School of Engineering, University of Guelph, Guelph, Canada, N1G 2W1

[wstiver@uoguelph.ca](mailto:wstiver@uoguelph.ca), fax 519-836-0227

Supercritical fluid extraction systems can be configured in a number of different ways and the operating conditions can span the full continuum of temperatures and pressures. Every combination presents differing solubilities and mass transfer behaviour and results in different cost. Optimal conditions for processing are rarely coincident with optimal conditions for maximum solubility.

For a typical supercritical fluid extraction (SFE) system, the behaviour of utility cost as a function of operating conditions and solute solubility is explored. Fifteen solutes representing a wide range of interests were highlighted for study. The solutes represent a range of compounds including polar and non-polar, of varying levels of solubility and of biological or environmental interest. The optimal operating conditions for the extractor and separation vessel seem to fall in a narrow band.

## INTRODUCTION

Supercritical Fluid Extraction (SFE) has many advantages due to the strong dependence a solute's solubility has on the operating temperature and pressure. This strong dependence means that the operating conditions for the extraction and separation vessels influence SFE recovery rates, selectivity and ultimately overall extraction costs.

Selecting the optimal conditions is a significant challenge but also represents a significant opportunity. In principle, the available choices represent a four-dimensional space that controls equipment capital costs, extraction rates through both the mass transfer coefficients and solubility and the utility costs for the system. The goal of this paper is to explore the solubility and utility cost component of this four-dimensional space. Fifteen solutes are studied over a full spectrum of vessel temperatures and pressures.

## METHODOLOGY

The utility costs for a SFE process are dependent on two factors. One, is the difference in the solute's concentration in the supercritical fluid as it leaves the extractor compared to the value leaving the separator. In this work, the solute's solubility has been assumed to be solute's concentration leaving each unit. The second factor is the utility requirements to recirculate a given amount of supercritical fluid around a closed loop process.

A solute's solubility at a vessel's operating conditions ( $T, P$ ) have been determined based on the correlation of Guigard and Stiver [1]. The correlation is a density-dependant solute solubility parameter approach and has been successful for a wide range of solutes and supercritical fluids.

The utility requirements include electrical and cooling water. In a typical SFE process, carbon dioxide flows from the extractor at supercritical conditions ( $T_E, P_E$ ) through an expansion valve that operates isoenthalpically ( $h_2 = h_E$ ) and reduces the carbon dioxide's pressure to the separator conditions ( $P_2 = P_S$ ). The expansion reduces the carbon dioxide's temperature ( $T_2 < T_E$ ) to a point that is frequently below the desired temperature in the separator. In order to correct this, the carbon dioxide is heated to reach the chosen separator temperature ( $T_3 = T_S$ ).

Following the separator, the carbon dioxide is compressed isoentropically ( $s_5 = s_3$ ) to the

chosen pressure for the extraction ( $P_5 = P_E$ ). The carbon dioxide exiting the compressor has increased in temperature ( $T_5 > T_S$ ) and generally requires cooling to reach the chosen extractor temperature ( $T_5 > T_E$ ). This cooling step is completed with water.

The calculation of the carbon dioxide's enthalpy and entropy as a function of the system's temperature and pressure is based on the modified Benedict-Webb-Rubin (mod-BWR) Equation-of-State with the parameters for carbon dioxide from McLinden et al. [2]. The upper temperature limit for these parameters is 440 K which is exceeded for some operating conditions using a single-staged compressor. When exceeded, a multi-staged compressor is used to ensure that properties of carbon dioxide are not calculated with temperatures greater than 440 K.

Atypical SFE process configurations and corresponding calculations arise when the pressures and temperatures do not follow the typical patterns. Some configurations recover the solute through temperature changes alone. In this case, the above calculations for the energy requirements associated with sensible heat effects still apply and the expansion and compression energy requirements are eliminated. Another alternate configuration has the pressure in the separator greater than the pressure in the extractor. In this case, the isentropic compression is completed following the extractor and the isoenthalpic expansion following the separator.

The total utility cost is the sum of the energy required for compression and heating and the water required for cooling. The cost of cooling water was set at \$1/m<sup>3</sup> with the flowrate of cooling water determined based on a 15 K temperature increase in this cooling water. The energy cost was set at \$0.1/kWh with the compressor assumed to be 100 % efficient.

A computer program was developed to complete the calculations. The program interfaced with two existing software packages. REFPROP [2] was used to determine the enthalpies and entropies of carbon dioxide. Solubilities were determined using Stiver and Rampley [3]. The optimization procedure occurred in two stages. In the first stage, the cost of extraction is calculated at every combination of temperature and pressure within the range 300 K to 355 K and 5 MPa to 40 MPa at a resolution of 5 K and 2.5 MPa for each of the extractor and separator. The second stage performs a similar task but uses the optimum extractor and separator conditions returned by the first stage and a finer resolution of 1 K and 1 MPa.

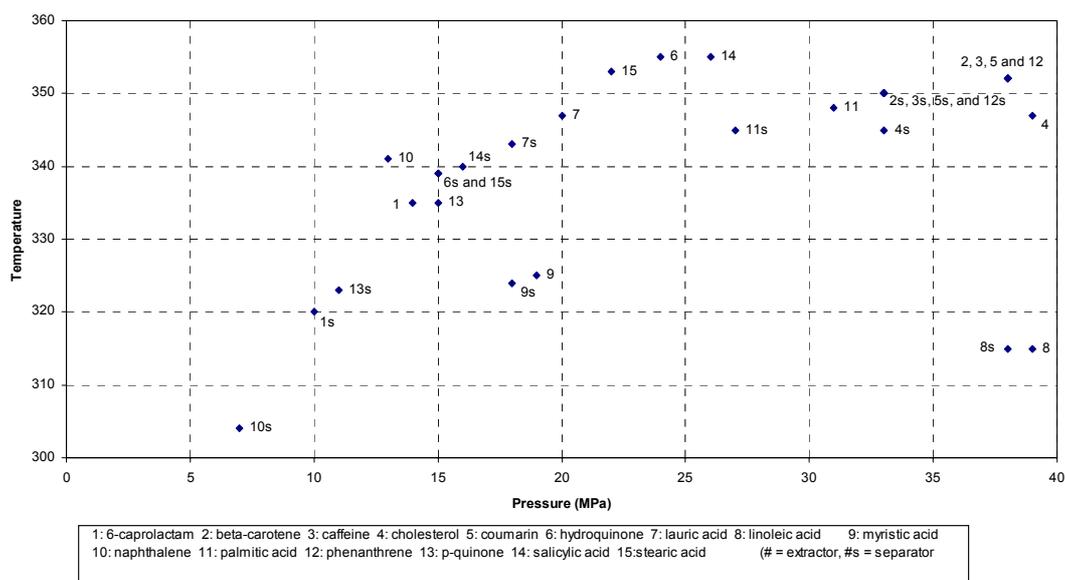
Table 1 identifies the fifteen solutes selected for study in this paper together with their necessary physical-chemical properties, coefficients for their solubility parameter determination and the solubility data reference. These fifteen solutes should be sufficient to explore the utility costs as a function of operating conditions.

## RESULTS & DISCUSSION

Table 1 provides the calculated optimal operating conditions and the minimum utility costs for the fifteen solutes. Minimum utility costs range from 0.003 to 30 \$/kg reflecting differences in the inherent solubility of the solutes. Figure 1 illustrates the optimal conditions for each of the fifteen solutes.

The optimal extractor and separator operating conditions are relatively close together for a given solute. The optimal conditions result from two competing forces. Maximizing the solute recovered per mole of recirculating solvent while minimizing energy required to recirculate the solvent. The former prefers maximum differences in the conditions while the later prefers minimal differences. The result is a compromise with the gap between conditions dependent on the specific solute as illustrated in Figure 1.

The optimal extractor condition does not coincide with the maximum in solubility for any of the fifteen solutes. Although solubility tends to increase with increasing pressure, the rate of



**Figure 1:** Optimal Operating Conditions

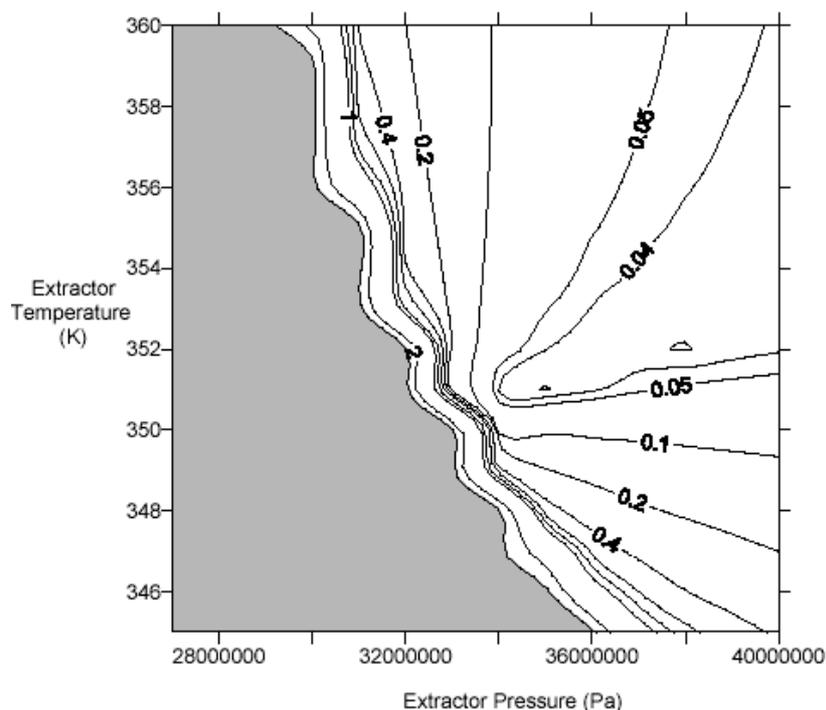
increase is fairly small at higher pressures. At these higher pressures, the magnitude of the solubility increase is not sufficient to justify the increasing energy requirements.

The relative relationship between the extractor and the separator's operating conditions is fairly consistent across the fifteen solutes. Generally, the separator is at slightly lower pressure and slightly lower temperatures. No case was found in which the separator condition was optimal at a higher pressure or at a higher temperature.

An interesting trend is illustrated in Figure 1. It appears that the optimal conditions for 14 of the 15 solutes follows a slightly curved band or region of pressure-temperature combinations. This would suggest that experimental and pilot work should focus in this region. Linoleic acid is the only exception. Linoleic acid has the lowest melting point and is the only solute that is a liquid under ambient conditions.

Figure 2 illustrates the iso-cost contour lines for  $\beta$ -carotene generated using the experimental solubilities published by Mendes et al. [5]. The figure is for a fixed set of separator operating conditions (350 K and 33 MPa; optimal separator conditions) and a range of extractor temperatures and pressures. The shaded region on the lower left side is the region in which  $\beta$ -carotene's solubility under the extractor's conditions is less than the solubility at the separator conditions. The steep set of contour lines on the edge of the shaded region is evidence that if the solubility in the extractor and separator are only marginally different the process conditions will not be cost effective. Further inspection of the figure indicates a widening valley of minimum cost that is the ideal region to consider operating the supercritical process from the perspective of utility costs alone. Utility costs in this valley are low and they tend to be relatively stable.

Figure 3 is similar to Figure 2 except that the extractor conditions are now fixed and the separator conditions are varied. The iso-contour lines are generated using the same experimental data set published by Mendes et al. [5]. The shaded region in the upper right-hand corner now indicates conditions in which the solubility is higher in the separator than in the extractor. The steep set of contours near the shaded region again represents a solubility difference that is too small to be cost effective. Finally a minimum cost region, just removed from the set of steep



**Figure 2:**  $\beta$ -Carotene Iso-cost lines for Separator Conditions of 350 K, 33 MPa.

contours, that would be the ideal region to operate from a utility cost standpoint. This low cost valley approximately follows the optimal cost band evident in Figure 1.

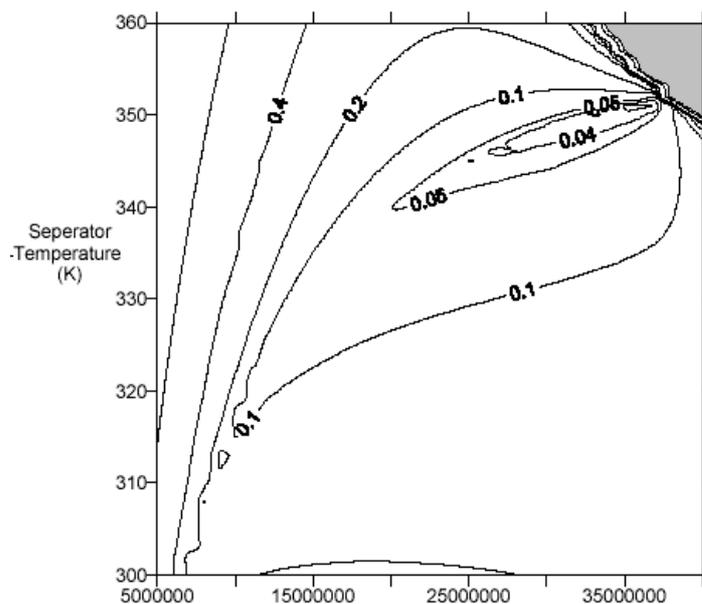
Figures 2 and 3 is indicative of the norm for all of the solutes studied in this paper where the separator operating conditions are held constant while the extractor's are varied. The basic shape observed is consistent for each of the solutes studied.

It is important to realise that these calculated results have been derived from experimental solubility data. For all fifteen solutes the quantity of solubility data available is not sufficient to map the entire temperature and pressure grid that has been the domain of this analysis. This forces the analysis to rely on extrapolation of the solubility data using the correlation. Extrapolation increases uncertainty. For this reason, it would be inappropriate to over interpret any single cost value or any single optimal operating conditions. The overall trends and the overall consistency of the fifteen solutes is less dependent on the individual solute's extrapolation. These trends can be treated with greater confidence.

These optimal conditions reflect utility costs alone. The optimal band observed in Figure 1 will likely shift if capital costs were included. Including capital costs adds several additional complexities and uncertainties particularly in relation to mass transfer limitations.

## CONCLUSIONS

The optimal SFE operating conditions have been explored for fifteen solutes. The minimum utility costs ranged from 0.003 to 30 \$/kg. The optimal conditions for fourteen of the fifteen solutes fall in a fairly narrow band. The optimal separator condition tends to be slightly lower in temperature and in pressure relative to the optimal extractor condition.



**Figure 3:**  $\beta$ -Carotene Iso-cost lines for Extractor  
Conditions of 352 K, 38 MPa.

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**Table 1:** Solutes, their properties, their optimal conditions and their utility cost

solute	MWt (g/mol)	$\Delta H_{\text{fus}}$ (J/mol)	$T_m$ (K)	$v_L$ (cm <sup>3</sup> /mol)	Guigard-Stiver Power Fit Parameters					Extractor Conditions		Separator Conditions		Total Cost (\$/kg)
					A	B	C	AARD (%)	ref	$T_E$ (K)	$P_E$ (MPa)	$T_S$ (K)	$P_S$ (MPa)	
6-caprolactum	113.16	16096	341	162.0	9.20	14.32	0.6784	10.	[4]	335	14	320	10	0.037
beta-carotene	536.88	56000	456	536.9	13.11	10.59	1.404	10.	[5]	352	38	350	33	29.
caffeine	194.19	21118	511	157.9	17.41	8.57	1.4805	5.3	[6]	352	38	350	33	0.45
cholesterol	386.65	26293	422	375	10.74	11.73	0.7882	24.	[7]	347	39	345	33	0.086
coumarin	149.14	19140	344	109	11.55	16.87	0.5401	53.	[8]	352	38	350	33	0.11
hydroquinone	110.11	27100	443	82.7	19.55	13.78	1.0885	6.9	[9]	355	24	339	15	9.1
lauric acid	200.32	36650	317	227	16.04	8.03	1.7355	12.	[10]	347	20	343	18	0.0030
linoleic acid	280.45	55745	268	311	16.21	10.10	1.3573	34.	[10]	315	39	315	38	0.0043
myristic acid	228.37	45100	327.6	265	8.37	15.29	0.8304	7.2	[11]	325	19	324	18	0.0096
naphthalene	128.17	19100	353.2	125	15.53	10.67	1.9301	16.	[12]	341	13	304	7	0.051
palmitic acid	256.42	54935	335.9	301	17.56	7.24	2.9049	2.1	[11]	348	31	345	27	0.0054
phenanthrene	178.23	16463	372.2	182	13.42	12.41	1.1548	5.4	[13]	352	38	350	33	0.074
p-quinone	108.09	18450	386	82.0	13.97	11.45	0.7337	16.	[9]	335	15	323	11	0.038
salicylic acid	138.12	19585	432	95.7	19.17	10.41	1.4209	15.	[14]	355	26	340	16	0.46
stearic acid	284.48	61300	342.8	336	7.48	16.86	1.0116	7.2	[7]	353	22	339	15	0.0098