

SEPARATION OF HEAVY OILS USING SUPERCRITICAL FLUIDS

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INTRODUCTION

This paper focuses on separations of heavy oils and materials from synthetic fuels which are of sufficiently high molecular weight that they cannot be separated by distillation. There is, however, the possibility of fractionating these heavy oils by solvent extraction. This is done commercially by use of low molecular weight paraffins to extract a high-quality deasphalted oil (DAO) from the low-quality asphaltene fraction.

Since 1960 consideration has been given to potential use of supercritical gases as solvents for the separation of heavy oils. A general review of this field is given by Funk and Irani (1). This paper addresses the important question of selectivity and in particular examines the selectivity differences which one can obtain with supercritical gases versus conventional liquid solvents.

New experimental data are presented for the supercritical extraction of heavy oils using carbon dioxide and CO₂/solvent mixtures and also phase-equilibrium data for extraction with liquid solvents to allow rational interpretation of differences in selectivity.

This paper also presents a non-analytical, statistically based technique for interpretation of experimental data which can complement the numerous analytical models (2,3,4) available for analysis of supercritical extraction data.

DEASPALTING -- LIQUID SOLVENTS AND SUPERCRITICAL GASES

Table 1 presents a summary of the properties of typical heavy oils which are separated by solvent deasphalting using paraffinic solvents. This extraction aims to produce an oil which is free of the very high molecular weight asphaltenes, lower in metals content (Ni, V, Fe), and with minimal quantities of heteromolecules (N, S, O).

Figure 1 shows a schematic diagram of a typical solvent deasphalting process. It is basically a countercurrent liquid-liquid extraction. The paraffinic solvent is recovered by vaporization or advanced heat-integrated schemes which recover the solvent as a supercritical fluid (5).

Selectivity in this extraction shows very interesting behavior. It is completely predictable, and predictable over a wide variety of liquid solvents. Figure 2 shows this "universal" curve for vanadium with Athabasca bitumen as the heavy oil. One sees that the fraction of vanadium in the oil fraction is a simple function of the yield of extract. Other similar curves hold for other major properties (S, N, O) and this behavior is found with a variety of other heavy oils (Arabian Long, Tia Juana Resid, Jobo).

Figure 2 doesn't just include extraction with paraffins but a variety of other solvent types (ketones, alcohols, amines, aldehydes, etc.). It also holds for mixed solvent systems (6). These data were obtained at ambient temperature and with a solvent/oil ratio of 10.

A key question in the field of supercritical extraction is whether supercritical gases can show selectivity behavior which deviates from the type of universal curve shown in Figure 2.

A detailed study of the use of supercritical propane (1) showed that there are no differences in selectivity when the extraction is compared at the same yield (the correlating factor in Figure 2). The experimental data presented in Figure 3 illustrate this point. First, simple comparison of liquid propane at 60°C and 7.72 MPa with supercritical propane extraction at 115°C (T_c for propane = 97°C) does show very different behavior. The yield curves are shown in Figure 3 and the extraction at supercritical conditions gives metal concentrations 20-25% of those obtained with liquid propane. However, pressure is a key variable in the supercritical extraction and increasing the pressure increases the DAO solubility; at a pressure of 10.34 MPa, the yield curve matches the curve for extraction with liquid propane. For these conditions (115°C, 10.34 MPa), the extracted DAO has extremely similar properties (Ni, V, Fe, S, O, N) to the extraction at sub-critical conditions.

This study with propane suggests that for paraffins, there is no inherent selectivity to extracting with the solvent as a supercritical gas although it may appear so if results are not compared at equal yield of DAO.

EXTRACTION WITH SUPERCRITICAL CO₂ AND CO₂/SOLVENT MIXTURES

Figure 4 presents a schematic diagram of the extraction unit used for these experimental studies. The gas goes from the cylinder to a compressor which brings it to the system pressure. The extractor is stainless steel and the gas enters the bottom of the extractor and is dispersed by a stainless steel grid. The extractor contains the feedstock oil, which is distributed over glass beads to provide good contact between gaseous solvent and the oil. The extracted material and solvent leave the top of the extractor, the pressure is reduced and extracted material is collected for analysis. The basic design of the unit is similar to that proposed by Reid (7) and Eckert (8).

Figure 5 presents experimental data on the extraction of a heavy Boscan crude with supercritical CO₂ at 40°C (T_c for carbon dioxide = 31°C) from 5 to 25 MPa. Carbon dioxide was selected for this study because it is widely used in supercritical extraction and also because it may give selectivity (weakly acidic and with a quadruple moment). The results in Figure 5 show that CO₂ is a very poor solvent for heavy oils compared to propane. Even pressures of 24 MPa give only 2% oil in the extract phase (comparable results with propane (1) give 20-30% oil in the extract phase).

The selectivity results are very interesting and are summarized in Table 2. These data show a high selectivity for basic nitrogen compounds such as pyridines and quinolines. For example, the β (extract/feed) of the pyridines is 85. This is a very high selectivity and is very different for the low selectivities shown in the universal curve (Figure 2). It does seem expected that the acidic CO₂ would tend to preferentially extract the basic compounds. It is also interesting that some other classes of compounds (thiophenes and phenols) were also preferentially extracted. On the other hand, CO₂ shows no selectivity for saturated or aromatic hydrocarbons. The data in Table 2 were obtained by GC-MS analysis of the feed and extract samples.

Limited experimental studies examined the use of entrainers

(ethanol, heptane) to increase oil yield during the supercritical extraction with CO₂. For these studies the solvents were added to the oil feedstock in the extractor. For both ethanol and heptane, 10% solvent added to the oil gave a 3-5 times increase in yield, however the type of selectivity shown in Table 2 disappeared and for each compound type, selectivities were less than 5 (similar to Figure 2). Thus for CO₂ extraction, entrainers may be used to dramatically increase yield but at the price of selectivity.

DATA ANALYSIS FOR SUPERCRITICAL EXTRACTION OF HEAVY OILS

There are presently available very powerful statistical techniques to design experiments in such a way that the data can be reduced to provide quantitative measures of key variables and interactions between variables (9). These statistical techniques are used in a wide variety of other technologies which deal with complex systems but have not found application in the area of supercritical extraction. This type of statistical analysis could complement the more traditional analytical modeling of supercritical phenomena.

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Table 1. Properties of Typical Heavy Oils

	Athabasca Bitumen	Cold Lake Crude	Jobo Crude
Composition, Wt. %			
Sulfur	4.9	4.29	3.87
Nitrogen	0.45	0.46	0.68
Oxygen	0.9	0.5	0.57
H/C Atomic Ratio	1.52	1.49	1.49
Metals, WPPM			
Nickel	80	61	90
Vanadium	250	180	455
Asphaltenes, Wt. %	14.2	17.9	17.7
1050°F+, Wt. %	47.3	45.2	49.4

**Table 2. Analysis of Oil Extracted With
Supercritical Carbon Dioxide at 40°C**

Compound Type	Feed	100, atm	150, atm	200, atm
Pyridines	0.02	1.69	1.31	0.56
Quinolines	0.41	1.55	1.54	1.51
Thiophenes	0.001	0.39	0.48	0.66
Phenols	0.01	0.63	0.52	0.26
Saturated Hydrocarbons	42.94	41.35	41.21	40.37
Aromatic Hydrocarbons	23.34	26.25	26.85	27.15

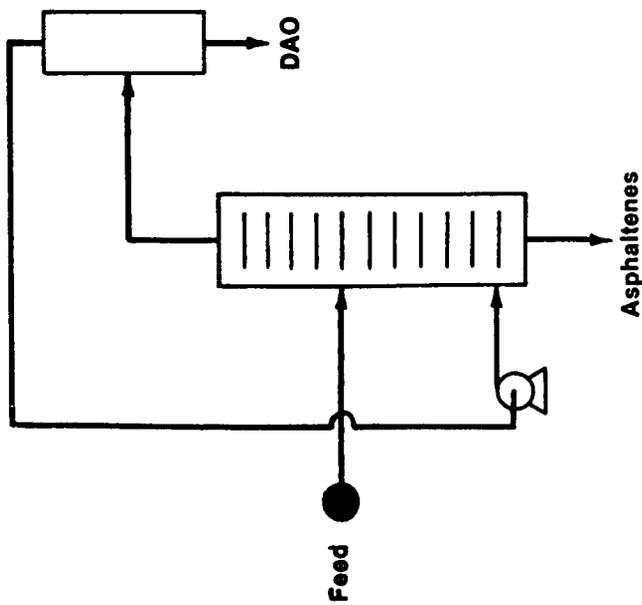


Figure 1. Schematic Diagram of a Solvent Deasphalting Process

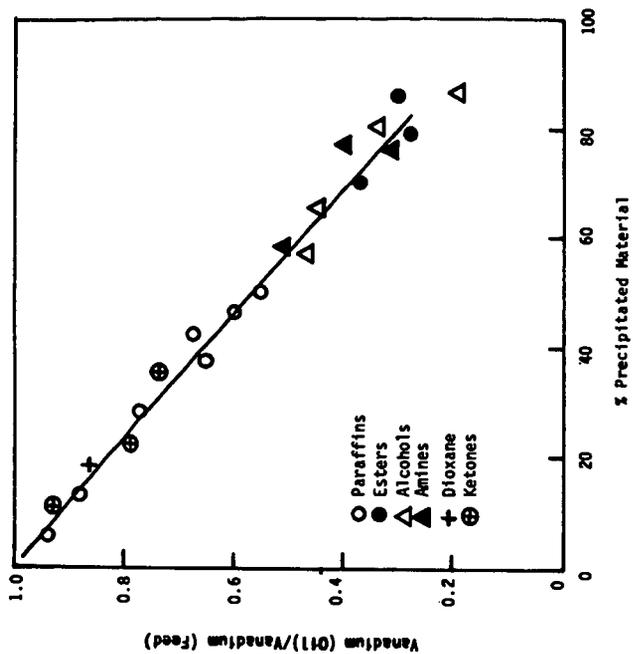


Figure 2. Correlation of Vanadium Content With Extraction Yield

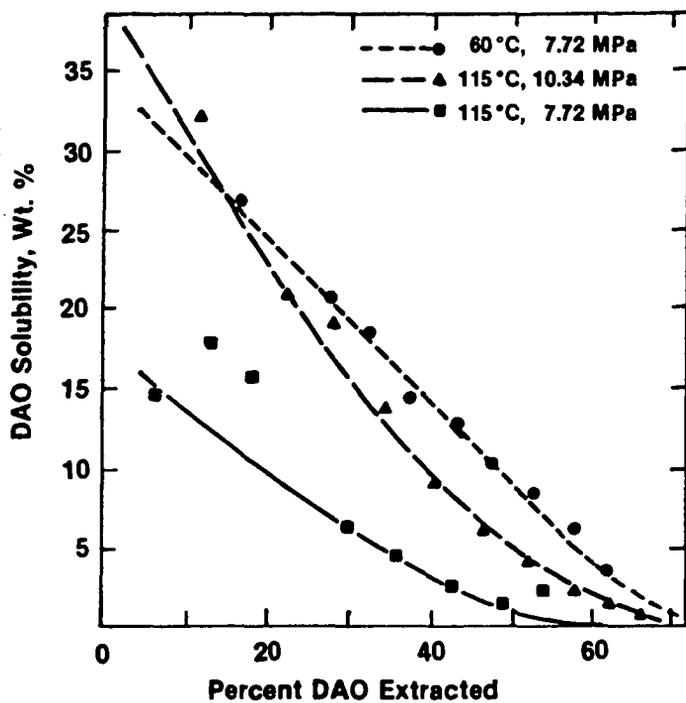


Figure 3. Extraction of Arabian Long Heavy Oil With Liquid and Supercritical Propane

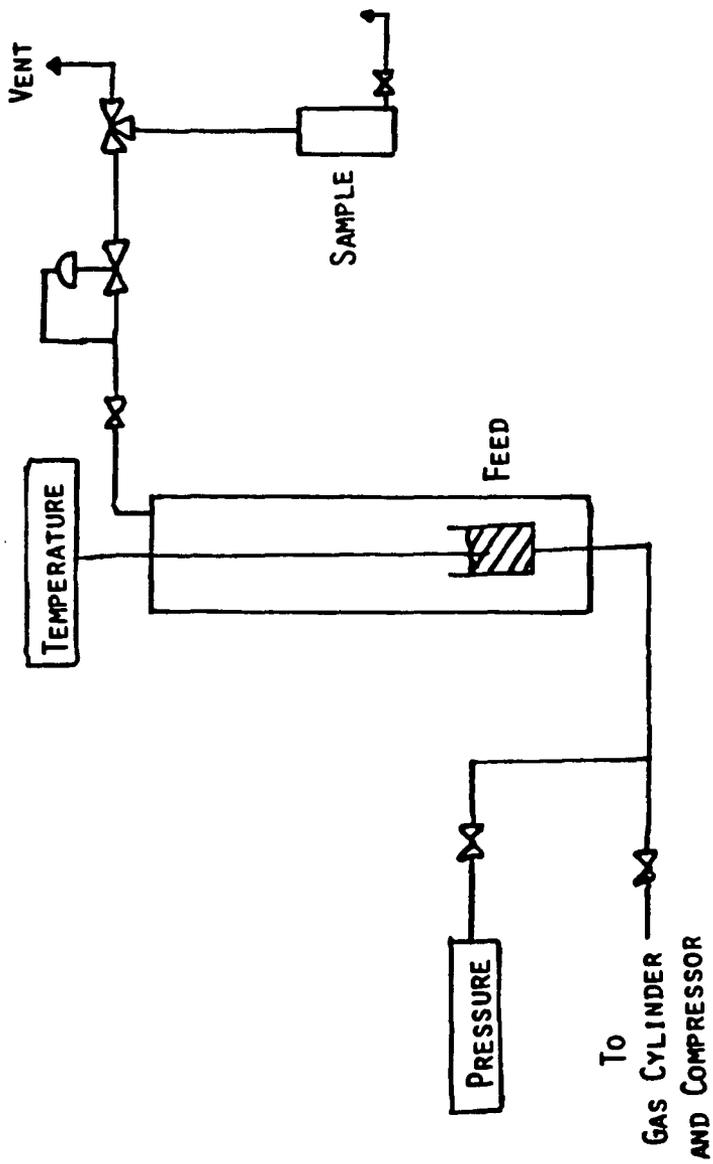


Figure 4. Experimental Unit for Supercritical Extraction With CO₂ and CO₂/Solvent Mixtures

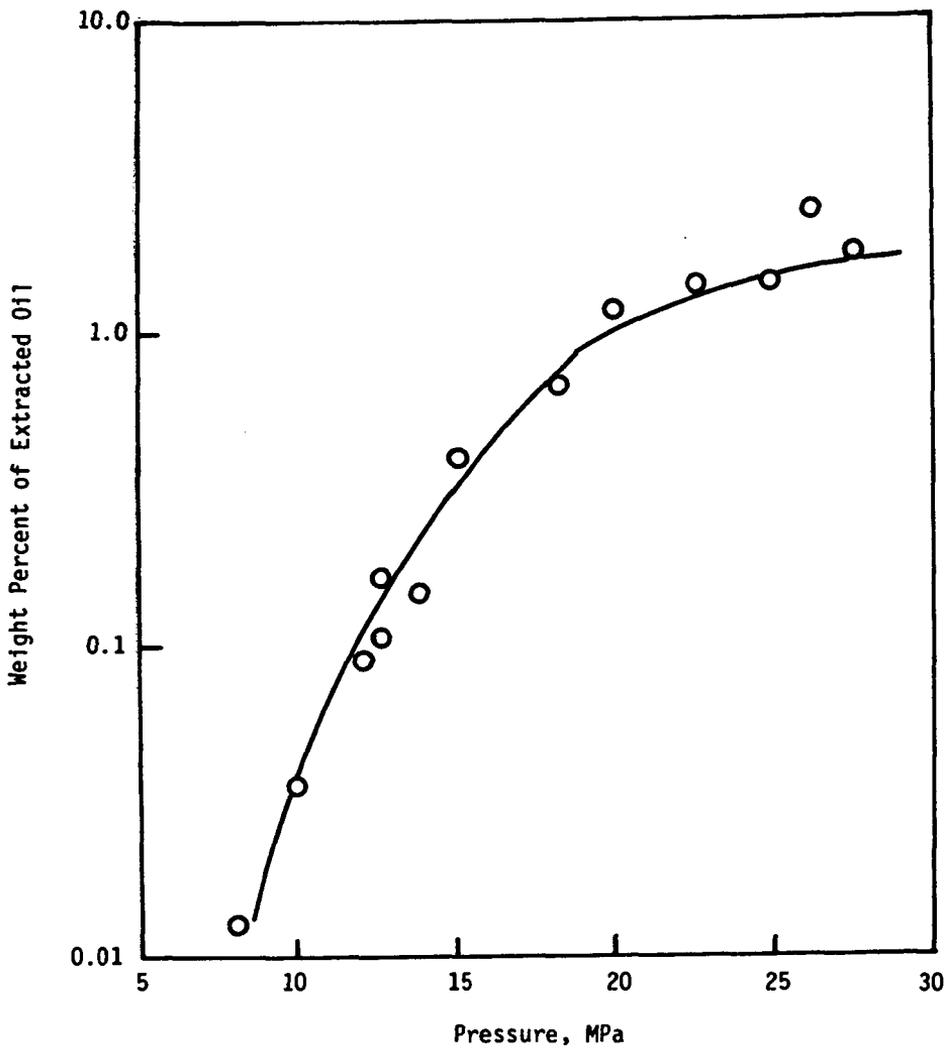


Figure 5. Supercritical Extraction of Boscan Crude With CO₂ at 40°C