DEVELOPMENT AND DESIGN OF A HIGH PRESSURE CARBON DIOXIDE SYSTEM FOR THE SEPARATION OF HAZARDOUS CONTAMINANTS FROM NON-HAZARDOUS DEBRIS*

SAND-95--1601

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ABSTRACT

Under the Department of Energy (DOE)/United States Air Force (USAF) Memorandum of Understanding, a system is being designed that will use high pressure carbon dioxide for the separation of oils, greases, and solvents from non-hazardous solid waste. The contaminants are dissolved into the high pressure carbon dioxide and precipitated out upon depressurization. The carbon dioxide solvent can then be recycled for continued use. Excellent extraction capability for common manufacturing oils, greases, and solvents has been measured. It has been observed that extraction performance follows the dilution model if a constant flow system is used. The solvents tested are extremely soluble and have been extracted to 100% under both liquid and mild supercritical carbon dioxide conditions. These data are being used to design a 200 liter extraction system.

KEY WORDS: Supercritical, Carbon dioxide, Cleaning

1. INTRODUCTION

Large quantities of solid wastes such as rags, kimwipes, swabs, coveralls, gloves, *etc*., contaminated with oils, greases and hazardous solvents are generated by industry and the government. At present, these materials must be treated as hazardous waste, and the cost of disposal of such large volumes of hazardous materials is high. If the hazardous components (oils, greases and solvents) could be segregated from the much larger bulk of non-hazardous material, then these solid materials could potentially be handled as sanitary waste at significant cost savings. AlliedSignal KCP, a typical DOE manufacturing site, spent several hundred thousand dollars in CY92 for disposal of contaminated solid wastes. If the hazardous and non-hazardous components could be segregated and disposed of separately, costs would be reduced significantly.

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*This work was performed in part at AlliedSignal Inc., Kansas City Division, supported by the U.S. Department of Energy under contract number DE-AC04-76-DP00613, and in part at Sandia National Laboratories, supported by the U.S. Department of Energy under contract number DE-AC04-94AL85000.

The objective of this joint AlliedSignal KCP/Sandia National Laboratories project is to demonstrate the feasibility of using high pressure carbon dioxide to segregate hazardous oils, greases, and organic solvents from non-hazardous solid waste such as rags, wipes, swabs, coveralls, gloves, *etc*. Carbon dioxide possesses many of the characteristics desired in an "environmentally acceptable" solvent system. It is nontoxic, inexpensive, and recyclable. A schematic of an ideal cleaning apparatus is shown in Figure 1. Contaminants dissolved in the CO_2 solvent are separated out by expansion of the fluid to a lower pressure where CO_2 is a gas and the dissolved materials precipitate out (usually as a liquid or solid). The gaseous CO_2 can then be recompressed and recycled. The cycle describing a typical supercritical extraction is schematically represented on the carbon dioxide phase diagram in Figure 2.

2. EXPERIMENTAL EQUIPMENT AND METHODS

The experimental activity currently in progress is directed at determining the extractability and solubility of the major oils, greases, and solvents. Both the "extractability" and the "solubility" of the contaminant affect the cleaning/recycle process. Solubility is a thermodynamic equilibrium property of the solvent-contaminant system. Extractability, on the other hand, is the amount of contaminant that can be removed from the substrate. It is affected by the chemical nature of the contaminant and substrate, and the mass transfer in the cleaning system. The extractability of a contaminant cannot exceed its solubility. The solubility as a function of pressure and temperature determines the conditions that the separator must be operated at in order to achieve a given level of carbon dioxide purity in the recycle. Since the pressure drop must be recovered in the recompression step, the economics of the process are greatly affected by the separator conditions.

At Sandia, a high pressure view cell is used to measure the thermodynamic equilibrium solubility of contaminants in high pressure carbon dioxide. Pressures up to 68.9 MPa and temperatures of 373 K can be achieved. Visual determination of the phase condition of a contaminant/CO_2 mixture as a function of temperature and pressure is made. The dew point (contaminant solubility in CO_2) or bubble point (CO_2 solubility in contaminant) of the mixture can be measured. From this data, equilibrium phase plots can be constructed as a function of concentration and solubility information obtained.

At AlliedSignal KCP, a recycling high pressure carbon dioxide cleaning system was used to measure the extractability of oils, greases, and solvents from laboratory paper wipes as a function of the pressure, temperature, flowrate, and total mass flow of supercritical carbon dioxide. The recirculating/recycle feature allows continual exposure of the contaminated solids to clean carbon dioxide for as long as necessary without consuming large amounts of CO_2. For example, at 358 K and 32.4 MPa, the cleaning system contains only 7 kg of CO_2, but in a one hour run, 27 kg of fluid are circulated through extraction vessel. At the end of a cleaning cycle, the clean solids are removed from the extractor to be reused or discarded as non-hazardous waste. The oils/greases/solvents, now in concentrated form, are drained from the separator and disposed of as hazardous waste.

Oils, greases, and typical solvents common to DOE/USAF facilities were identified. The list included 131 oils and greases in use at the Kansas City Plant and USAF bases. These were sorted by type and by monthly usage in order to allow a priority ranking for the experimental work. Hydraulic and cutting oils were most commonly used. A similar organic solvent list contained 29 solvents in use within DOE and USAF facilities consisting mostly of cleaning solvents, paint thinners, and aircraft fuels. Isopropanol, methyl ethyl ketone, and perchloroethylene were the most commonly used solvents. It was assumed that those materials used most were most likely to appear as contaminants on waste can, rag debris.

3. DISCUSSION OF EXPERIMENTAL RESULTS

Twenty-five of the most commonly used oils identified above were surveyed for solubility and extractability in supercritical CO_2. The results are very encouraging -- in most cases the percent contaminant removal is > 99%. Only the most viscous, high molecular weight oils result in lower removals, and even these typically exceed 96% at 348 K and 32.4 MPa. Mild supercritical conditions such as 318 K and 17.9 MPa are adequate for essentially complete removal of most of the contaminants. The additives present in commercial oils are not typically removed and a stain remains on the rag. The amount of remaining contaminant is extremely small and is typically composed of viscosity modifiers such as highly branched polyisobutylene and polymeric butyl azelate esters. These polymeric materials are not normally considered to be hazardous substances.

Viscosity is the key physical property governing the solubility and extractability of the contaminant oils. Figure 3 shows the equilibrium solubility of three oils of differing viscosity in supercritical carbon dioxide. Of the three oils, the lowest viscosity oil has greater solubility. These numbers, however, are extremely low -- less than 5 wt%. Nonetheless, as was mentioned above, high removal values were achievable given adequate CO_2 exposure. This effect was explored further by comparing the extraction data to the dilution model. The dilution, or constant stirred tank reactor, model assumes the contaminant is completely soluble, the input and output flowrates are equal, and the vessel fluid is instantaneously homogeneous as dilution of the contaminant occurs:

$$Q_n = Q_o \exp(-n)$$

where Q_n is the contaminant concentration after n extractor volume exchanges by CO_2 and Q_o is the initial contaminant concentration. Figure 4 compares the extraction of five oils with the dilution model over a range of extraction exchange volumes. Note that the high viscosity oil is removed more slowly than the dilution model predicts. This is due to its small solubility. The other four oils follow or exceed the ideal dilution model. Any deviations from the dilution model are due to the fact that residual oil in the extractor condenses on the walls as well as on the paper wipes upon decompression. Basically, at an initial contaminant loading of approximately 0.2 wt.%, 95% of the contaminant is removed within three volume exchanges. Clearly, the effect of loading on the extraction rate must be assessed. This data, however, will be highly apparatus specific because mass transfer will dominate.

Extraction values were also measured in liquid CO_2. Any reduction in the working pressure of the system translates directly into reduced capital equipment costs. There will be some decrease in the operating costs of a full scale system, although the major savings are in the equipment. Again, extraction of the oils to high values -- > 90% -- was observed provided enough CO_2 exposure was provided. In order to explore the effect of viscosity in liquid CO_2, the extractability of oils of varying viscosity at 10 MPa, 301 K and 5.3 vessel volume exchanges was tested. The results are shown in Figure 5. Excellent contaminant removal in liquid CO_2 can be achieved for oil viscosities up to 300. The lower percent removals of the highly viscous oils does not mean they cannot be removed, but simply that more than 5.3 vessel volume exchanges are required.

The extraction of 22 common solvents have been measured at both supercritical (318 K, 17.9 MPa) and liquid (301K, 10 MPa). 5.3 vessel volume exchanges were used in all tests. At these conditions, the dilution model predicts a removal of at least 99.5%. All solvents were extracted to 100% under both liquid or supercritical conditions. Basically, the solvents are extremely soluble in high pressure CO_2. Solubility measurements made on these solvents demonstrate that 5% by weight can be dissolved in supercritical CO_2 at pressures less than 10.3 MPa at 318 K. Indeed, even in liquid CO_2, no phase separation is observed between the solvent and carbon dioxide until the gas-liquid phase separation is observed.

4. CONCLUSIONS

The experimental results clearly indicate that the concept of separating hazardous waste from non-hazardous solids using supercritical or liquid carbon dioxide is feasible. Of primary importance in designing the equipment necessary to perform this separation, is identification of the waste stream. If heavy, highly viscous oils are a large fraction, it may be more practical to operate at supercritical conditions. And while it has not been discussed in this paper, if solvents are a large fraction, then a distillation-type separator will be necessary since the high vapor pressure, highly soluble solvents cannot be separated from the carbon dioxide using a standard, cyclone-based, pressure reduction separator design. The solvent issue is important for several reasons: (1) if the solvent is not removed in the separator, the recycle system reaches an equilibrium saturation concentration; and (2) the solvents are more likely to present a worker safety issue and if the recycle system is saturated, solvent will be vented during the vessel depressurization and the worker will exposed when the vessel is opened. Identification of the waste stream is also necessary because there are contaminants for which this technique is unsuited. Cured epoxy, dried paints, heavy greases (the hydrocarbon component is removed leaving the inorganic soap), and polysulfides cannot be removed using either supercritical or liquid carbon dioxide.

A full-scale, 200 liter unit is being designed for the Waste Management Department at the AlliedSignal - Kansas City Plant. It will serve both as a rag recycle facility for the Kansas City Plant and a manufacturing-scale demonstration unit for other DOE plants, USAF and other military service facilities, and any other government or private agency interested. The present laboratory cleaning apparatus at AlliedSignal can be used to demonstrate the principle on actual solid waste, but does not have the capacity that a plant-wide unit would require. Design experiments using a “dish-washer” mode (static contact followed by draining) were performed and were found to be inadequate in removing the oils because of their low solubility. Little oil was required to saturate the extraction vessel contents. Additional experiments indicated the importance of agitation in removing low solubility, oil contamination.

In conclusion, hazardous contaminants can be separated from non-hazardous debris using high pressure carbon dioxide. Indeed, in most cases, liquid carbon dioxide is adequate. The viscosity of oils is particularly relevant in determining the necessary contact time. Solvents can be easily extracted from the debris, but require special attention in the separation step.

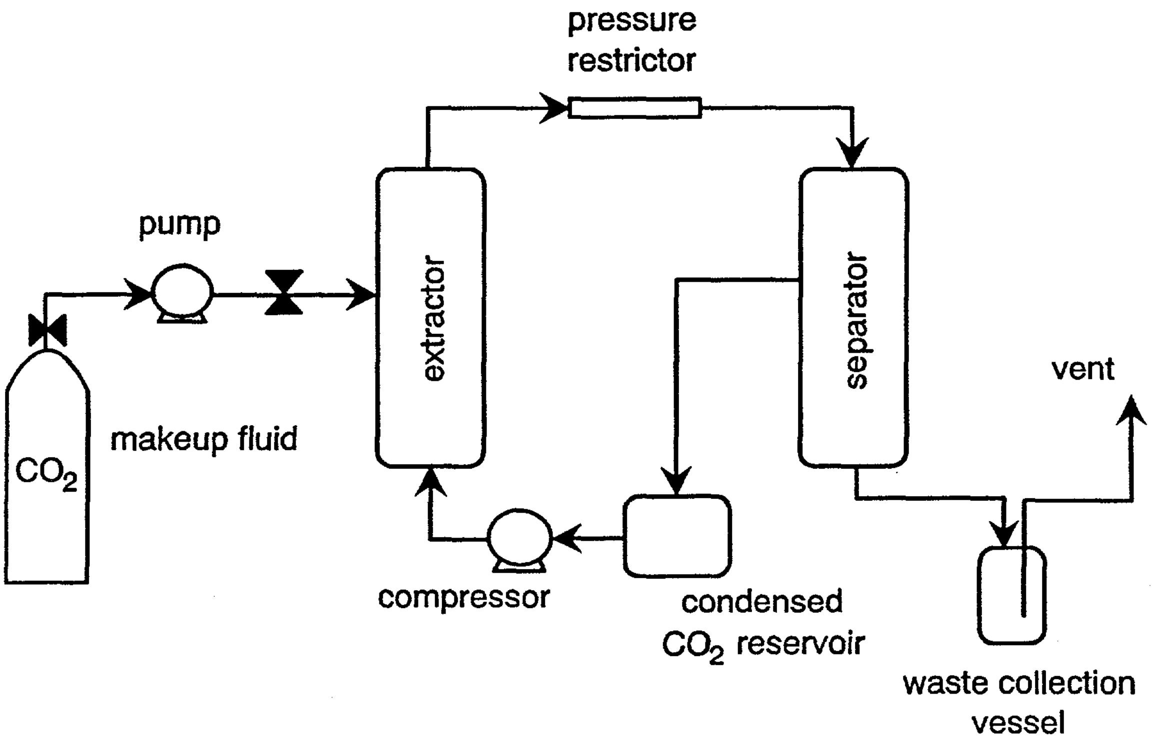

Figure 1. Ideal high pressure carbon dioxide cleaning apparatus.

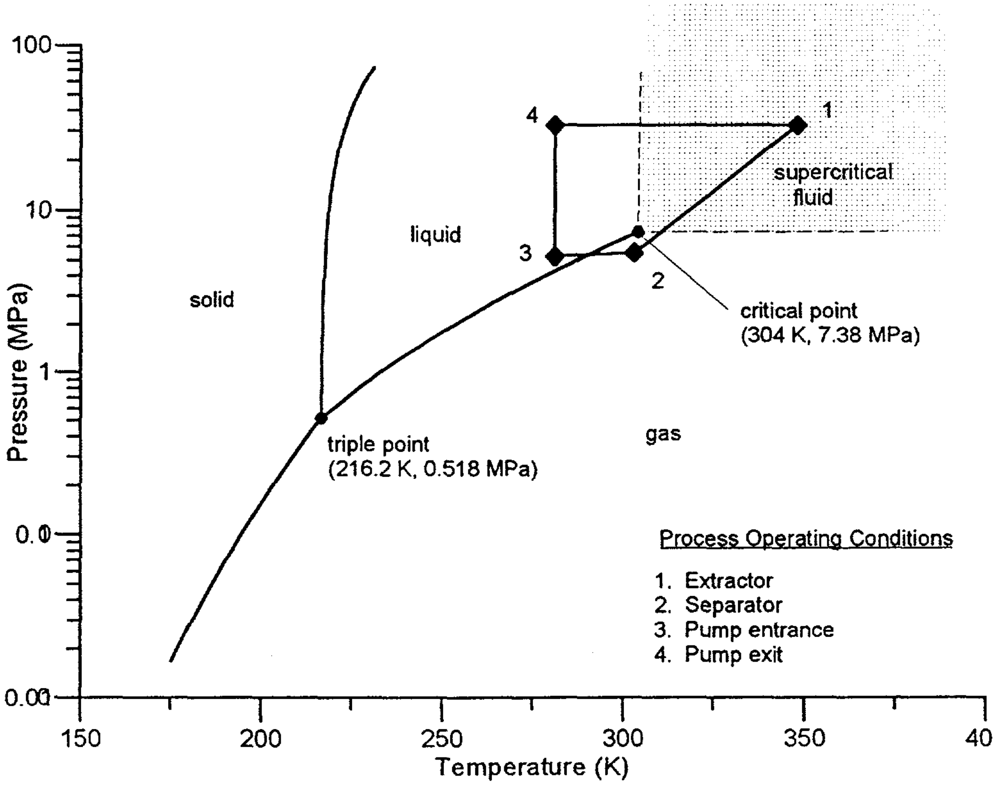

Figure 2. Operating cycle for supercritical CO_2 extraction system

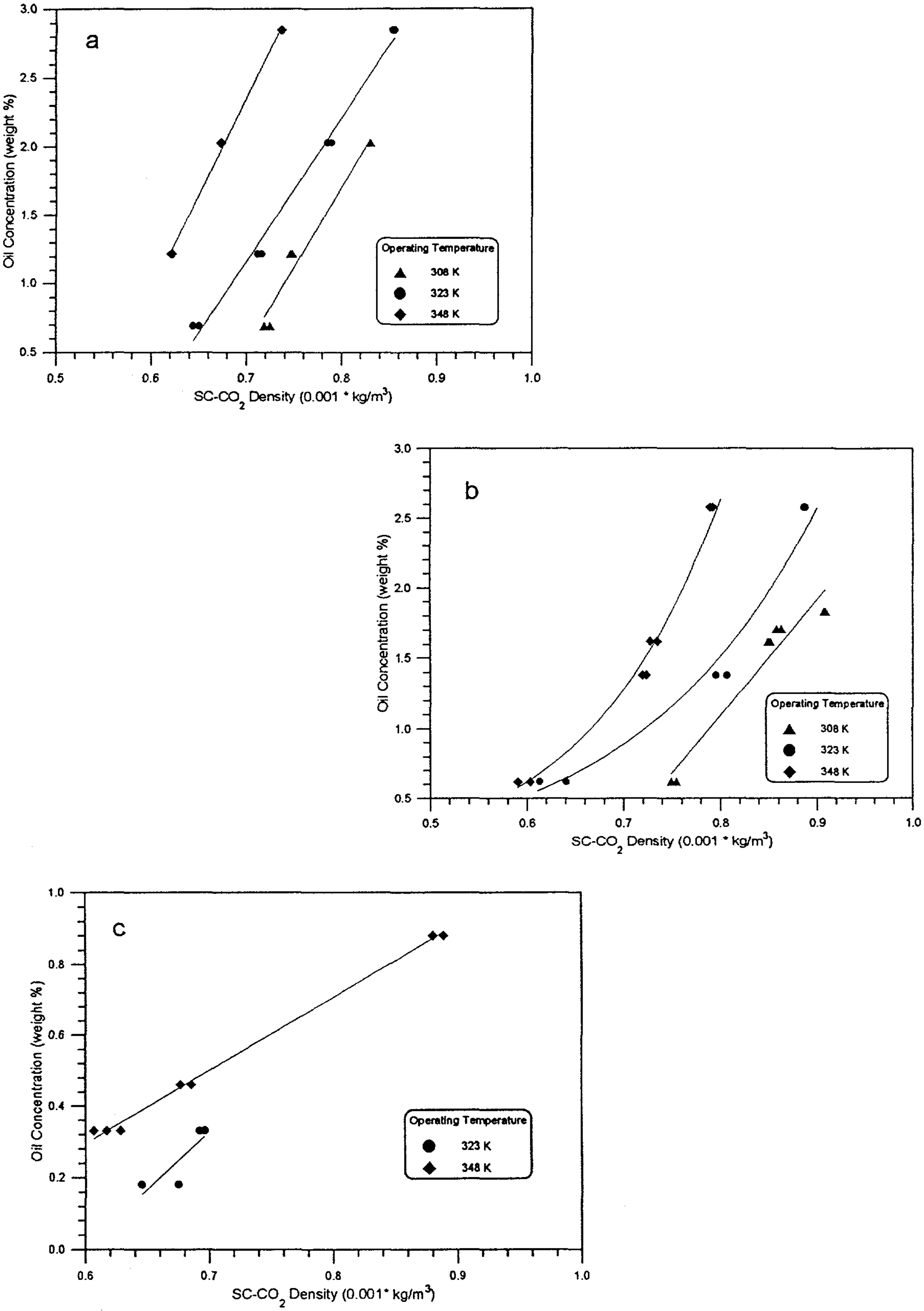

Figure 3. Solubility of (a) hydraulic oil Mobil vis 145-160, (b) hydraulic oil Mobil vis 300-320, and (c) oil Mobil DTE vis 1045-1165.

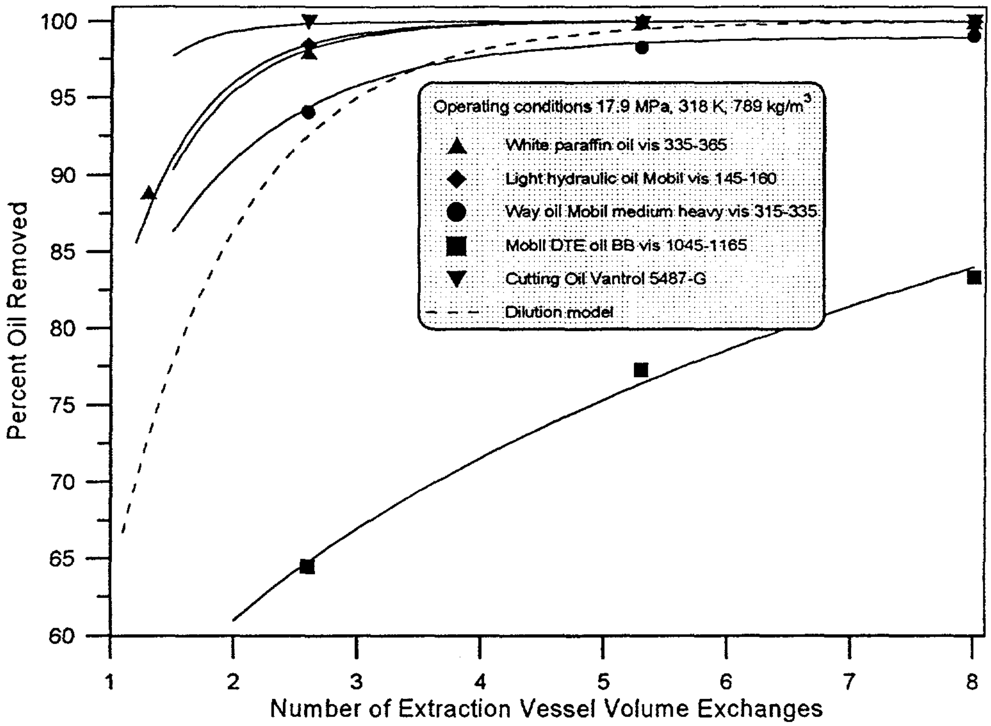

Figure 4. Percent oil removed by supercritical CO_2 as a function of vessel volume exchanges.

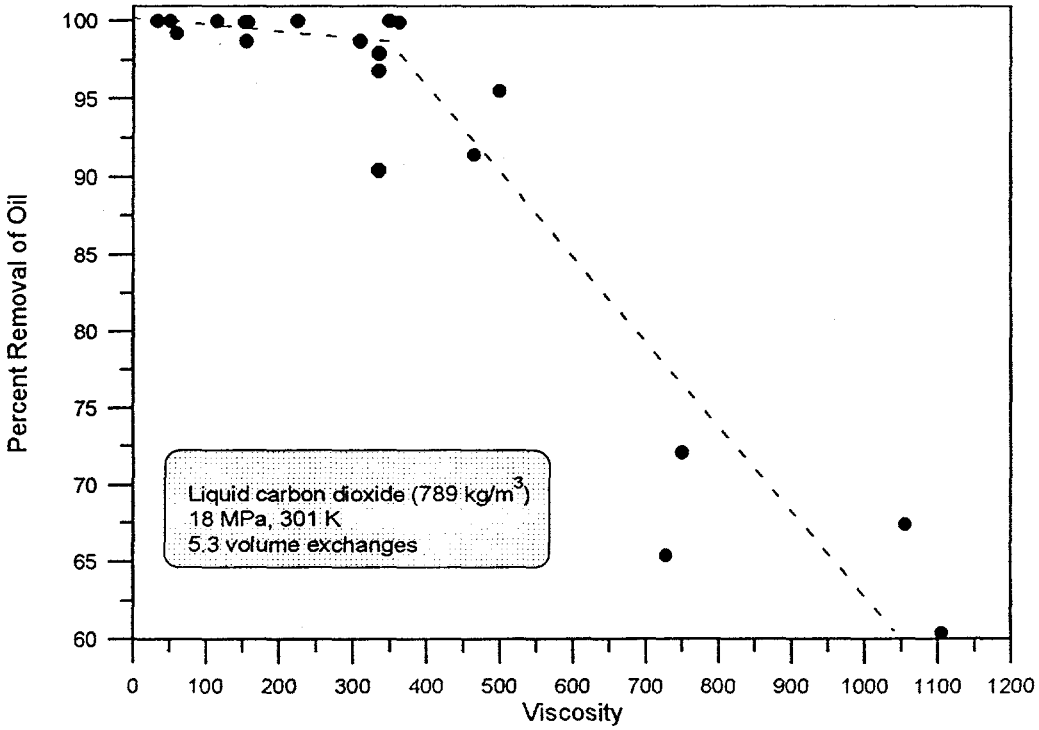

Figure 5. Percent oil removed by liquid CO_2 as a function of viscosity.