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# OIL, GREASE, AND SOLVENT REMOVAL FROM SOLID WASTE USING SUPERCRITICAL CARBON DIOXIDE*

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## ABSTRACT

Supercritical carbon dioxide extraction is being explored as a waste minimization technique for separating oils, greases, and solvents from solid waste. The contaminants are dissolved into the supercritical fluid and precipitated out upon depressurization. The carbon dioxide solvent can then be recycled for continued use. Definitions of the temperature, pressure, flowrate, and potential co-solvents are required to establish the optimum conditions for hazardous contaminant removal. Excellent extractive capability for common manufacturing oils, greases, and solvents has been observed in both supercritical and liquid carbon dioxide.

## 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 nonhazardous material, then these solid materials could potentially be handled as sanitary waste, at a significant cost savings.

Under the Department of Energy (DOE)/United States Air Force (USAF) Memorandum of Understanding, the objective of this joint AlliedSignal Kansas City Plant (KCP)/Sandia National Laboratories project is to demonstrate the feasibility of using supercritical carbon dioxide (SC-$CO_2$) to segregate hazardous oils, greases, and organic solvents from nonhazardous solid waste such as rags, wipes, swabs, coveralls, gloves, etc. Supercritical carbon dioxide possesses many of the characteristics desired in an "environmentally acceptable" solvent system. It is nontoxic, inexpensive, and recyclable.

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Carbon dioxide possesses a moderate critical temperature (304 K) and pressure (7.38 MPa). At 310 K and pressures greater than 13.78 MPa, the density is greater than 800 $kg/m^3$. A schematic of an ideal cleaning apparatus is shown in Figure 1. Contaminants dissolved in the supercritical $CO_2$ solvent are separated out by expansion of the fluid to a subcritical pressure where $CO_2$ is a gas. The dissolved materials precipitate out (usually as a liquid or solid). The gaseous $CO_2$ can then be recompressed and recycled.

Efforts to minimize the amount of hazardous waste requiring disposal are not only environmentally and socially conscious but also minimize the "cradle-to-grave" liability associated with disposal. Regulatory agencies are beginning to allow the use of technology to separate hazardous waste from debris. Not only is the waste minimized due to the segregation of the nonhazardous debris, but if the "debris" can be recycled and reused a number of times before disposal, then sanitary landfill waste will also be minimized.

## EXPERIMENTAL EQUIPMENT

The experimental activity currently in progress is directed at determining the extractability and solubility of oils, greases, and solvents. These two phenomena -- "extractability" and "solubility" -- uniquely define the extraction process for a given contaminant. Solubility is a thermodynamic equilibrium property of the solvent-contaminant system. Extractability, on the other hand, is defined not only by the solvent and contaminant, but also by the substrate and the equipment. Mass transfer plays an important role in defining extractability. The extractability of a contaminant cannot exceed its solubility. The solubility as a function of pressure and temperature also determines the conditions at which the separator must be operated 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.

A high pressure view cell is used to measure the thermodynamic equilibrium solubility of contaminants in high pressure carbon dioxide. Pressures up to 69 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.

A recycling, high pressure carbon dioxide cleaning system was used to measure the extractability of oils, greases, and solvents from laboratory paper wipes. Measurements as a function of the pressure, temperature, flowrate, and total mass flow of supercritical carbon dioxide were made. Figure 2 shows the recirculating waste segregation process cycle on a $CO_2$ phase diagram for a supercritical extraction. The solid waste to be cleaned is placed in the extractor (position 1), and the SC-$CO_2$ flowing through the vessel dissolves the contaminants and carries them away. When the contaminant-laden supercritical fluid expands across the pressure restrictor into the separator (position 2), the dissolved material precipitates out and is left behind in the separator. The gaseous $CO_2$ is cooled, reliquified (position 3), and then repressurized (position 4) to be used again in the extractor. This recirculating feature allows continual exposure of the contaminated solids to clean supercritical fluid 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 the extraction vessel. At the end of a cleaning cycle, the clean solids are removed from the extractor to be reused or discarded as nonhazardous 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 AlliedSignal KCP and USAF bases. These were sorted by type and by monthly usage in order to allow a priority ranking for the experimental work. By far the most commonly used oils were hydraulic and cutting oils. A similar organic solvent list contained 29 solvents in use within DOE and USAF facilities. Cleaning solvents, paint thinners, and aircraft fuels made up most of the list. Isopropanol, methyl ethyl ketone, and perchloroethylene were the most commonly used solvents.

## DISCUSSION OF EXPERIMENTAL RESULTS

Solubility measurements in supercritical $CO_2$ were made on the most commonly used oils. The data for three oils of varying viscosity are shown in Figure 3. Several observations can be made. First, solubility decreased as the viscosity increased. Second, at a given $CO_2$ density, solubility increased as the temperature increased for a given oil. However, to achieve a given density at ever increasing temperatures also requires increased pressures. And third, the solubilities for any of the oils were rather low -- less than 5 wt.%. It is perhaps this last point that is key in understanding the extractability of oils.

In order to generate data that could potentially be transferred from one system to another, the extractor was modeled using the dilution equation (continuous stirred tank reactor). The dilution 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 with incoming pure $CO_2$:

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

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 extractability of five oils (100 - 1100 Saybolt viscosity) with the dilution model over a range of extraction exchange volumes at mild supercritical conditions (318 K, 18 MPa). For the less viscous oils, the dilution model works well. 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. The high viscosity oil, however, is removed more slowly than the dilution model predicts. This is due to the oil's extremely low solubility -- the assumptions stated above are not met. This data does not, however, imply that the technique fails for high viscosity oils. Figure 4 clearly indicates that the percent removal continues to increase with increased exposure to the $CO_2$ solvent. The effect of extractor loading -- particularly for the relatively insoluble oils -- must be assessed. "Dish washer" mode experiments for various oil contaminants have been performed in which the extractor is filled, held static, and then drained. The results have proven unsatisfactory -- particularly for the more highly viscous oils in which the solubility is extremely low. Contaminant loading is limited because once the vessel volume is saturated, no further extraction occurs. In this mode of operation, the extractability is limited by the vessel volume, contaminant solubility, and contaminant loading. The advantage of continuous flow operation is that these three factors, while they may affect the economics of the extraction, do not limit the extractability.

Twenty-five of the most commonly used oils at AlliedSignal KCP have been surveyed for solubility and extractability in SC-$CO_2$. The results are encouraging -- in most cases the percent contaminants removal is greater than 99%. Only the most viscous, high-molecular-weight oils result in lower removal, and for either increased $CO_2$ exposure or more severe conditions (e.g., 348 K, 32 MPa), even these typically exceed 96%. Mild supercritical conditions such as 318 K and 18 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.

The capital cost of high pressure equipment is a strong function of the maximum allowable working pressure (MAWP). For this reason, extractability was measured at *liquid* $CO_2$ conditions. The extractability of oils as a function of viscosity in liquid $CO_2$ at 10 MPa, 301 K, and 5.3 vessel volume exchanges is shown in Figure 5. Clearly, excellent contaminant removal in liquid $CO_2$ can be achieved for oil viscosities up to 300. Once again, the lower percent removals of the highly viscous oils simply means that more than 5.3 vessel volume exchanges will be required to achieve high removals.

The extraction of 22 common solvents has been measured at both mild supercritical (318 K, 18 MPa) and liquid (301 K, 10 MPa) conditions. The number of vessel volume exchanges was 5.3 in all tests. At these conditions, the dilution model predicts a removal of at least 99.5%. All solvents were extracted to 100%, at both liquid and supercritical conditions. 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.

## REGULATORY IMPLICATIONS

The disposal of hazardous solvents is regulated nationally, with additional local regulation possible. In the past, "treatment" of hazardous debris waste and separation into its hazardous and nonhazardous components was not allowed. However, there are now federal regulations covered in the Federal Register (Vol. 57, No. 168, August 28, 1992, *Land Disposal Restrictions for Newly Listed Wastes and Hazardous Debris*) that specify performance standards for the solvent separation of certain hazardous wastes from nonhazardous debris. As is noted in the Federal Register, the philosophy is as follows (Section V.D.1): "...It is not normally the debris itself that is hazardous, but rather hazardous waste that is contaminating the debris. Thus, the goal of treatment should be to destroy or remove the contamination (if possible) and if this is achieved, to dispose of the cleaned debris as a nonhazardous waste..." "Performance" standards are established. The requirements for liquid solvent extraction are 15 minutes contact between the debris and solvent, and the contaminant must be soluble to at least 5% by weight in the solvent. The requirements for vapor phase solvent extraction are identical except 60 minutes contact is specified. In each case it is assumed that the contaminants enter the solvent phase and are flushed away from the debris. Since a supercritical fluid is neither a liquid nor a gas by traditional definitions, but has solvation powers and densities similar to a liquid and transport properties similar to a gas, the application of this standard to SC-$CO_2$ would have to be ascertained. However, the performance requirements (time and solubility) can be met for most common hazardous solvents for either liquid or supercritical conditions. The regulation of oils and grease disposal is addressed primarily by the states, and the federal debris rule does not necessarily apply. The recycle of material -- the reuse of cleaned rags -- is considerably more straightforward than their disposal.

## CONCLUSIONS

The experimental results clearly indicate that the concept of separating hazardous waste from nonhazardous solids using supercritical or liquid carbon dioxide is feasible. Identification of the waste stream is of primary importance in designing the equipment necessary to perform this separation. 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 two reasons: (1) if the solvent is not removed in the separator, the recycle system reaches a saturation equilibrium concentration and no more solvent is removed from the solid waste; and (2) the solvents are more likely to present a worker safety issue -- if the recycle system is saturated, solvent will be vented during the vessel depressurization and the worker will be 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.

In conclusion, hazardous contaminants can be separated from nonhazardous 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.

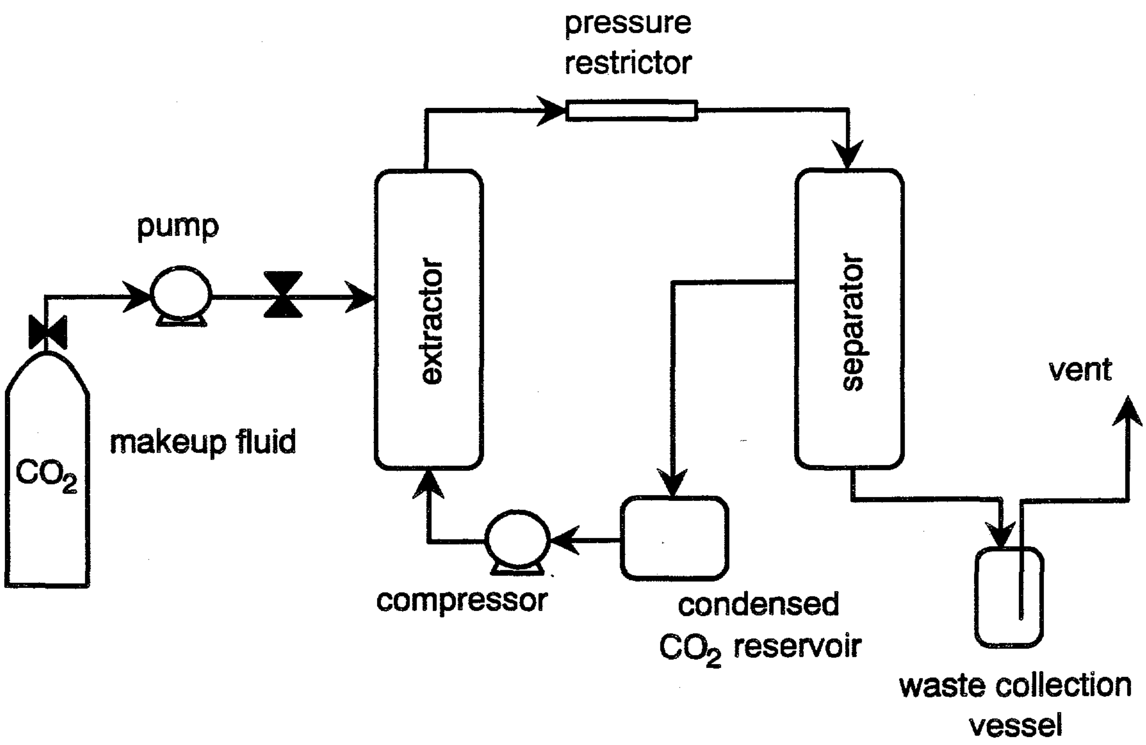

**Figure 1.** Ideal high pressure carbon dioxide cleaning apparatus.

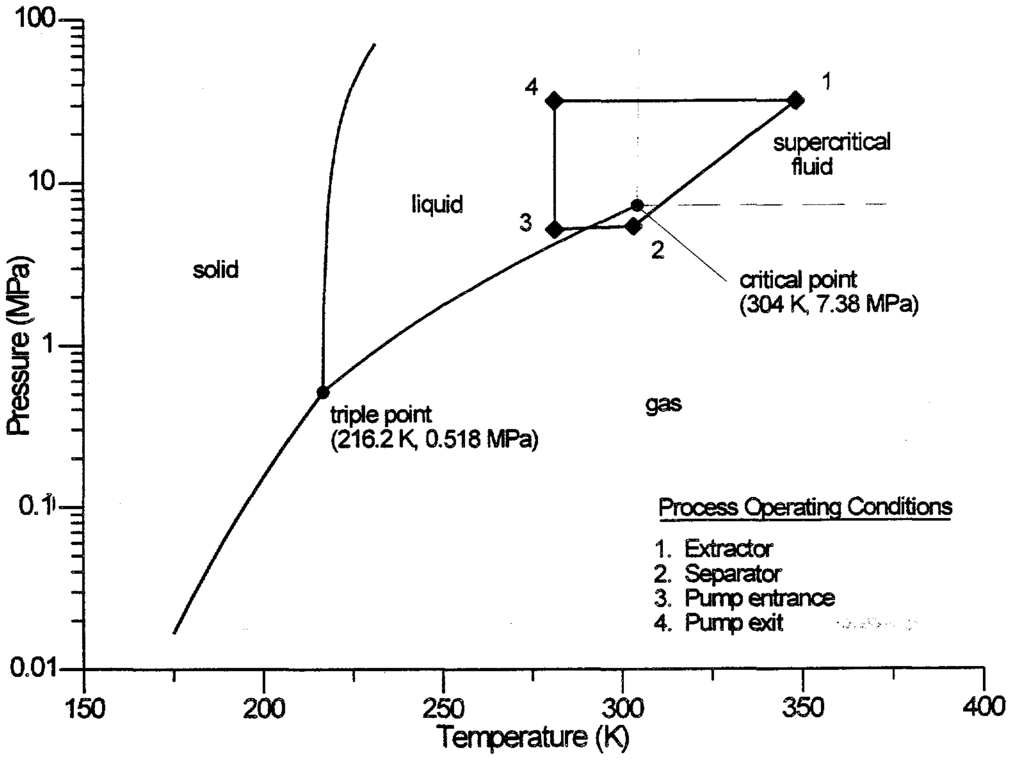

**Figure 2.** Operating cycle for supercritical $CO_2$ extraction system.

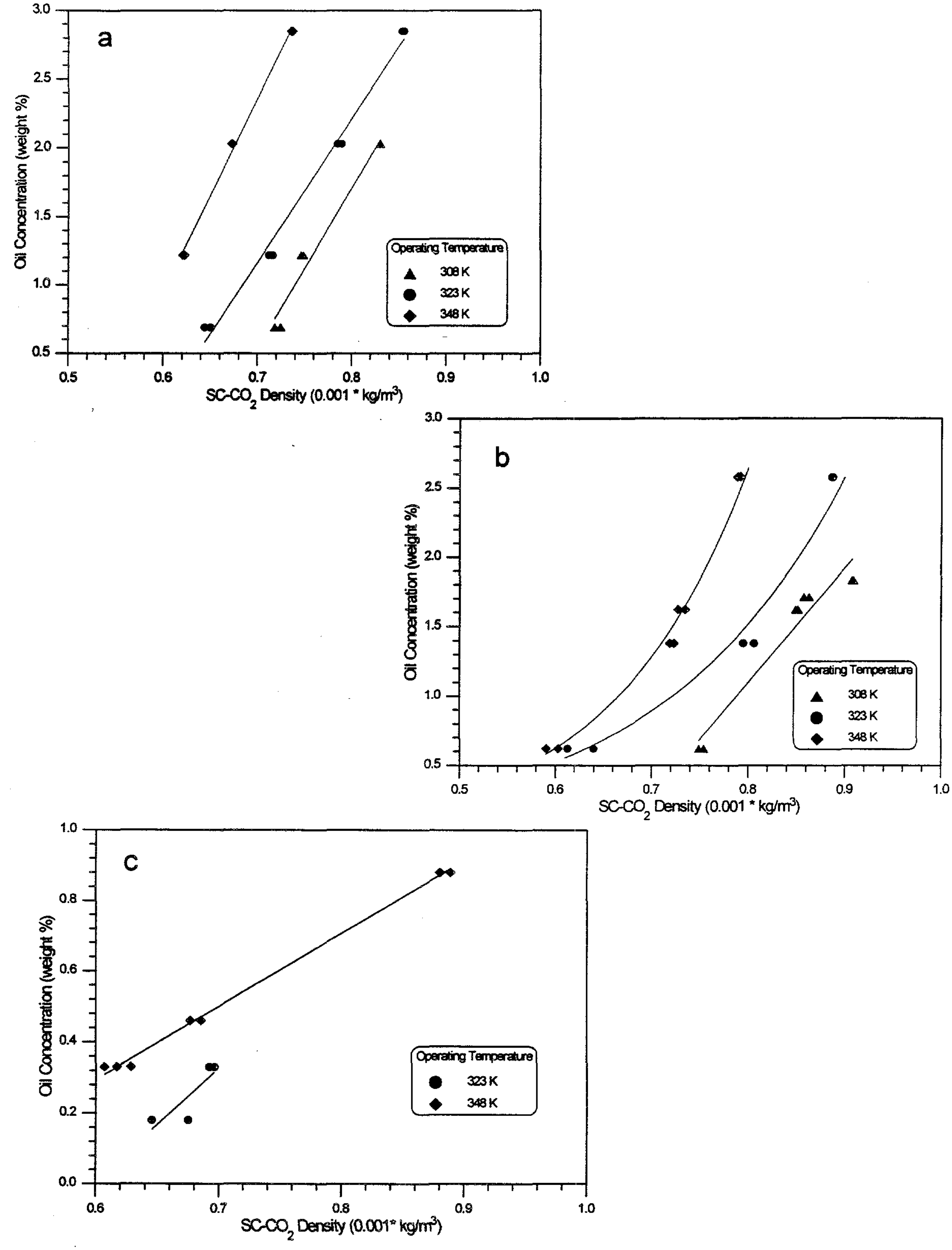

**Figure 3.** Solubility of (a) hydraulic oil Mobil vis 145-160, (b) hydraulic oil Mobil vis 300-320, and (c) oil Mobil DTE vis 1045-1165.

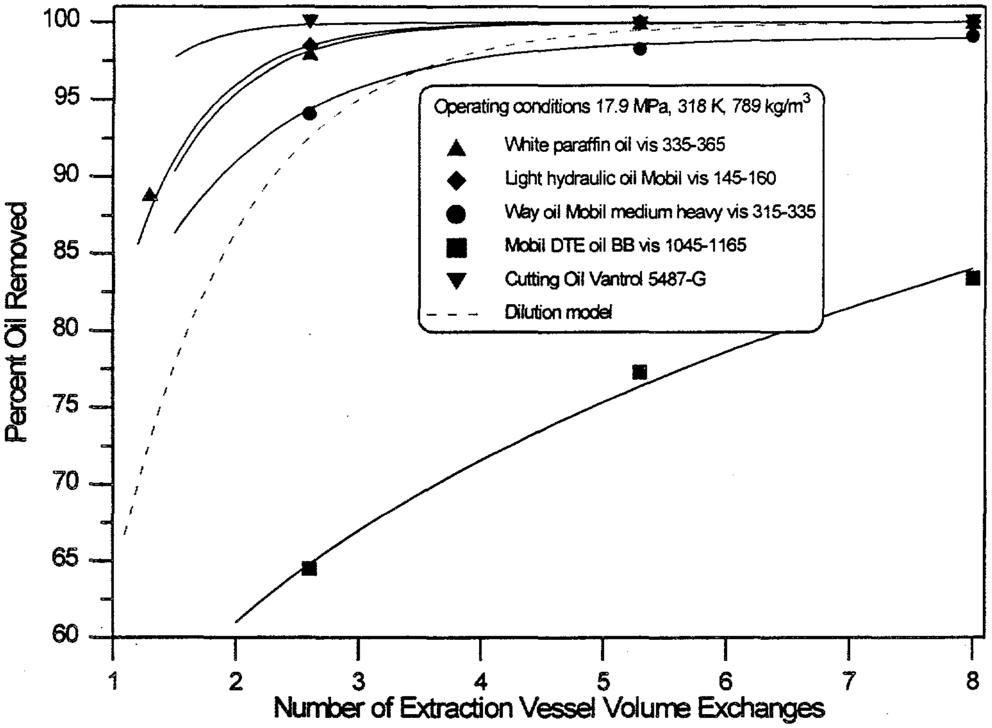

**Figure 4.** Percent oil removed by supercritical $CO_2$ as a function of vessel volume exchanges.

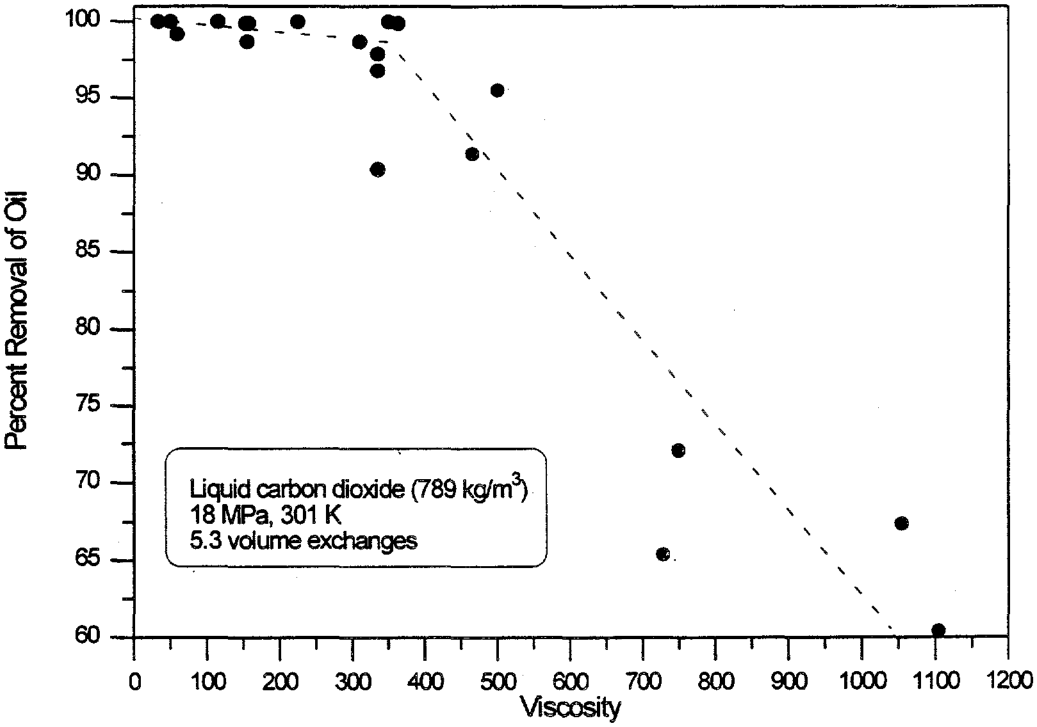

**Figure 5.** Percent oil removed by liquid $CO_2$ as a function of viscosity.