Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Schön, J. , Dahmen, N. , Schmieder, H. and Ebert, K.(1997) 'Separation of Oil-Contaminated Glass Grinds by Supercritical Fluid Extraction (SFE)', Separation Science and Technology, 32: 1, 883 — 897
To link to this Article: DOI: 10.1080/01496399708003235
URL: http://dx.doi.org/10.1080/01496399708003235

SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 883-897, 1997

SEPARATION OF OIL-CONTAMINATED GLASS GRINDS BY SUPERCRITICAL FLUID EXTRACTION (SFE)

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ABSTRACT

An extraction method is presented which relies on supercritical carbon dioxide as extractant. The development of the method and its demonstration in a bench-scale facility are described by the example of residues with high mineral oil and lead contents from machining optical glasses, the so-called glass grinds. By the extraction method, the oil can be recovered from the grinds in such a quality that direct recycling as grinding oil is possible.

INTRODUCTION

In Germany, oil-containing residues from metal and glass working, so-called grinds, are considered to be hazardous wastes and, therefore, require special and costly monitoring and disposal conditions. At present, the following ways are available for disposal of these wastes: at an oil content of more than 4%, thermal treatment, e.g., as addition to iron in the cement industry, or disposal by incineration with the oil acting as auxiliary fuel; at an oil content of less than 4%, there is the possibility of storing them on a hazardous waste site. The costs of

disposal are subjected to great variations; depending on the disposal path, costs are incurred of DM 800-3000 per ton of grinds.

According to an estimate by the Federal Environmental Office, 150,000 to 200,000 tons of these grinds are produced in Germany every year. The majority arise in machining medium- and high-alloyed steels or special materials with pure grinding and cutting oils used as cooling lubricants immiscible with water. Approximately 20-30% of them have high oil contents up to 50% grinding oil.

Several techniques are in the process of development and testing, respectively, in Germany by which oil separation through vacuum distillation or extraction using different solvents is to be accomplished. By all techniques, a quality of the end products is to be reached which allows their being recycled directly. The recovered oils are to be reusable as grinding and cutting oils, and the oil-free metal matrix is to be remeltable into the respective steels.

We will report now about an extraction process in which supercritical carbon dioxide is used as solvent. The process was developed for treatment of glass grinds with high mineral oil and lead contents arising in optical glass machining. The process has meanwhile proved to be excellently suited for the treatment of metal grinds as well (1).

The extraction properties of supercritical carbon dioxide and of other supercritical fluids have been known for many years already (3-9). Detailed investigations into the solubility of various substances in supercritical carbon dioxide have been conducted since the sixties. A compilation of the solubility values published until 1989 is contained, among others, in (2). Since the mid-seventies, supercritical carbon dioxide has also been used on a technical scale for the solvent-free extraction of natural products in the food and pharmaceutical industries (3-5). But there are only rare reports in the

literature about application on a technical scale of SFE in environmental technology (9-12).

We used carbon dioxide as the extractant in our method because, compared with other fluids, it is not toxic, not flammable, and does not form an explosive mixture with air. Considering the moderate critical data (critical temperature, 31.1°C; critical pressure, 73.8 bar), CO_2 can be readily converted into the supercritical state where the solvent power can be controlled over a wide range by variation of the pressure and temperature.

EXPERIMENTAL

Starting Material and Chemical Analysis

Real glass grinds arising in the production of optical glasses were used in process development. These wastes had been characterized by chemical analyses; besides SiO_2, the waste contained Pb (106.6 g/kg) and Zn (29.6 g/kg) in considerable amounts.

The glass grinds are thixotropic, pasty products which might contain up to 35 wt% grinding oil. The grain diameters of these particles extend over a range from 0.1-40 μm. The surface of the glass particles has been calculated, in addition, to be 4 m^2/ml. According to information from the supplier the grinding oil is a hydrogenated mineral oil—a mixture of about 60% paraffinic, 33% naphthenic, and 7% aromatic hydrocarbons. The oil is free of benzene, toluene, xylene, or higher polycyclic aromatics. Analysis of the main components by gas chromatography and mass spectrometry (GC-MS) yielded a bandwidth of hydrocarbons with 16 up to 36 C-atoms. Further information concerning the chemical nature and the amount of additives was not available from the supplier.

In the extraction experiments, complete splitting up and quantitative analysis of the individual components were not required to determine the

extraction efficiency because the total content of organic components in the material had been sufficiently characterized by the sum parameter of the total organic carbon (TOC). To speak of oil-free residues, a limiting value of less than 1% TOC was determined.

Measurement of Grinding Oil Solubility

The solubility behavior of the grinding oil in supercritical CO_2 was determined in a phase equilibrium apparatus (Sitec PH 251-500 K), applying the synthetic method. For this, a known amount of grinding oil was weighed into a thermostated autoclave equipped with sapphire window and a mobile piston, and was dissolved in supercritical CO_2, resulting in a homogeneous mixture. While the temperature was kept constant, the pressure was slowly lowered down to visible separation of the system. Contrary to the quick phase separation in binary mixtures, a clouding was observed, extending over a pressure range of 10 bar and more. To give an objective measure of phase separation in such a system, this clouding was detected via an optical system equipped with a photoelectric cell.

Extraction Experiments

The extraction behavior of the grinding oil as a function of the extraction parameters—pressure, temperature, CO_2 throughput, and flow velocity—was studied. The experiments were performed in two analytical SFE apparatuses: MPS 225, supplied by Suprex; and an equipment with a piston-type metering pump and automatic pressure control (Gilson M-308 and M-821). Samples of 0.5-1 g were extracted in a 1-ml extraction cell using supercritical CO_2. The cell can be passed by a continuous flow (dynamic extraction) or extraction is static by stopping the flow, or both modes can be coupled (static-dynamic extraction). The respective CO_2 throughput is

indicated by the pumps in ml CO_2, liquid. After extraction, the loaded CO_2 stream is expanded via a restrictor into a solvent reservoir which accommodates the oil precipitated. Depending on the solubility behavior of the extracted substance, precipitation or even plugging in the restrictor may result as a consequence of pressure reduction in the restrictor. In the experiments involving glass grinds, the variable restrictor (type Suprex Duraflow), whose cross section could be adapted to the respective requirements, proved to be less susceptible to trouble than the initially used integral fused silica restrictors.

In order to follow continuously the process of extraction, a flame ionization detector (FID) was connected as an on-line monitor downstream of the extraction cell via a split. A minor fraction of the loaded CO_2 stream passed into the detector. It was possible, in this way, to follow the hydrocarbon content in supercritical CO_2 until complete extraction (15). The effectivity of extraction was verified in the treated residue by measurement of the TOC content.

On the basis of the laboratory-scale measurements, an extraction flowsheet has been conceived for a bench-scale plant with batch sizes of 3-4 kg grinds. The bench-scale plant is represented schematically in Fig.1. The plant is equipped with a closed CO_2 cycle and allows a CO_2 flow rate of up to 30 kg/h at pressures up to 500 bar and maximum temperatures of 100°C. A diaphragm pump compresses the liquid CO_2 to the desired operating pressure and delivers the medium at the specified pump capacity via the heat exchanger into the extractor, accommodating the basket insert filled with the extracted material. The basket is closed on both ends with sintered metal plates and can be passed by a supercritical CO_2 flow either from bottom or from top. The supercritical CO_2 loaded with the extracted oil is expanded into the phase separator via a throttle valve. In the phase separator, a CO_2 liquid phase and a gaseous phase form at 60-70 bar pressure. The extracted

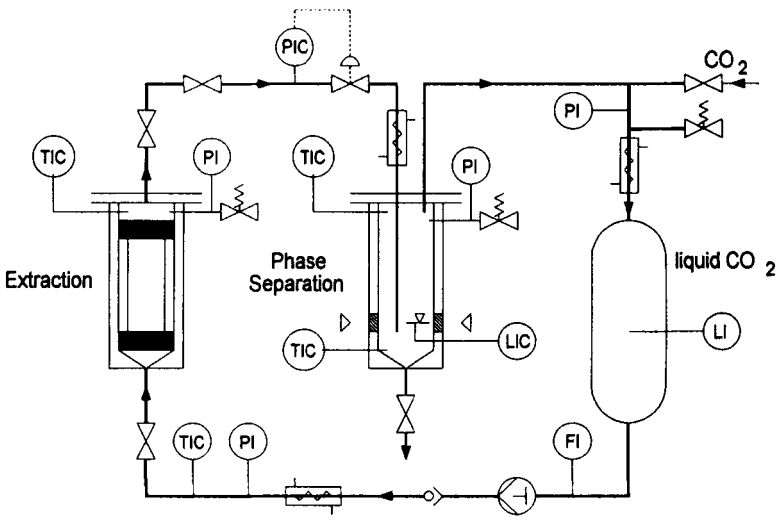

FIGURE 1. Bench-scale plant for supercritical fluid extraction

oil gets enriched in the liquid phase from which, after complete evaporation of the liquid CO_2, it is recovered as high-value grinding oil. The gas phase of the separator is continuously withdrawn, condensed, and returned into the cycle. In the experiments the oil content of the gas phase was found to be always less than 1 ppm.

RESULTS AND DISCUSSION

Solubility of Grinding Oil in Supercritical CO_2

The solubility data of the grinding oil determined by the synthetic method are presented in Fig.2. The measurements were made at 50°C. For comparison, the solubilities of the pure substances Squalan ($C_{30}H_{62}$) and Eicosan ($C_{20}H_{42}$) have been entered in addition in the figure as typical mineral oil representatives (14). The solubility of the grinding oil increases

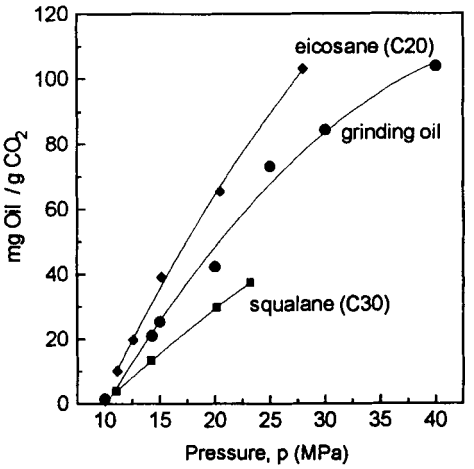

FIGURE 2. Solubility of grinding oil in supercritical CO_2

with the pressure; it lies between the solubilities of the two pure substances. Increase in pressure by the factor 4 produces an increase in solubility by nearly the factor 100; at 100 bar only a few milligrams of oil per gram of CO_2 are soluble, whereas at 400 bar about 110 mg oil/g CO_2 are dissolved.

A rise in temperature from 50°C to 80°C clearly lowered the solubility of the grinding oil. This effect is due to the decreasing density and the associated reduction in solvent power of supercritical CO_2 with increasing temperature. This relationship is evident from Fig.3, where the solubilities of the grinding oil at 50°C and 80°C have been plotted versus the respective solvent densities of CO_2 (13, 16). Within the accuracy of measurement, no significant difference has been found between the solubilities at the two temperatures.

Extraction of Grinding Oils in Supercritical CO_2

In terms of their consistency, the glass grinds are a solid oil suspension. The principal steps in extraction are deemed to be detachment

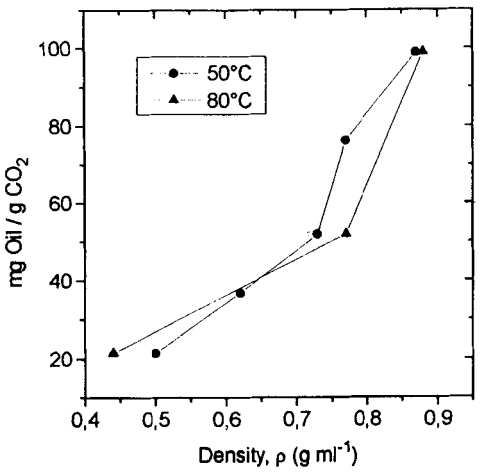

FIGURE 3. Solubility in dependence of density

of the oil from the surface of the glass particles and its removal by the fluid phase. The solubility of the oil had been determined with the synthetic method under static conditions. By contrast, most of the extractions are made in the dynamic mode; therefore, the influence of the flow rate on the effectivity of oil extraction was investigated more profoundly.

The influence of the flow rate at 100 bar and 50°C is shown in Fig.4 for flows of 0.2 and 1.7 ml/min. The course of extraction is plotted versus the CO_2 volume throughput. In the first phase of extraction (<40 ml CO_2), the differences in flow rates do not produce any effect. However, with ongoing extraction, the yield observed was smaller for the higher flow rate and the same CO_2 throughput. The observed dependency of oil extraction on the dwell time indicates that the rate of dissolution of oil in the range of densities investigated constitutes the rate-determining step in extraction of the glass grind, which has been confirmed by the experiments on static-dynamic extraction (see Fig.7).

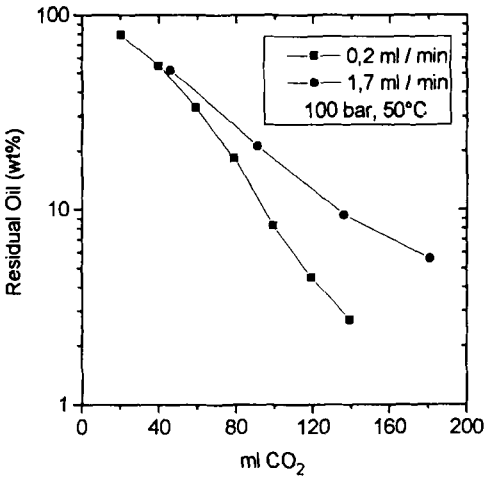

FIGURE 4. Extraction efficiency for different flow rates

The influence of pressure on the extraction yield is visible from Fig.5. The extractions are performed at a flow rate of 0.5 ml/min. At 300 bar, after a throughput of 20 ml CO_2, more than 95% of the oil has been extracted. For an extraction of 80% to be achieved, only 15 ml are required at 200 bar, but about 80 ml at 100 bar.

The residual oil left in the material is of interest with a view to technical-scale application of the method. These residues have been plotted in Fig.6 versus the specific CO_2 throughput in g CO_2/ g of material. At 100 bar the residue approaches, but very slowly, the specified value of 1%, whereas at 300 bar this is attained after a throughput of only 70 g/g. The curve at 200 bar was plotted, too, in order to show once more the influence of the flow rate; in the range up to 30 g CO_2/g the extraction proceeded at a rate of 0.3 ml/min., whereas the subsequent flatter course of the plot (throughputs 30-90 g CO_2 per g of material) results from extraction at a rate of about 1 ml/min. A last extraction step at 400 bar and 0.3 ml/min. flow rate

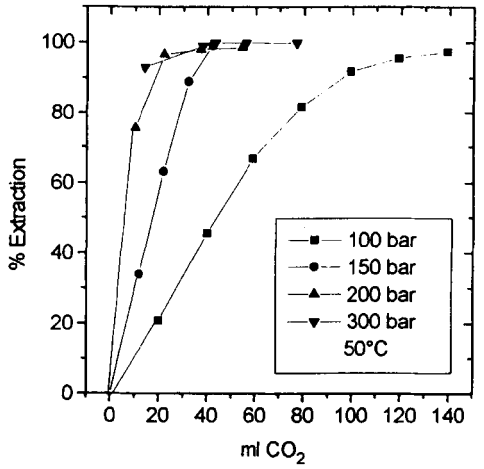

FIGURE 5. Extraction efficiency for different pressures

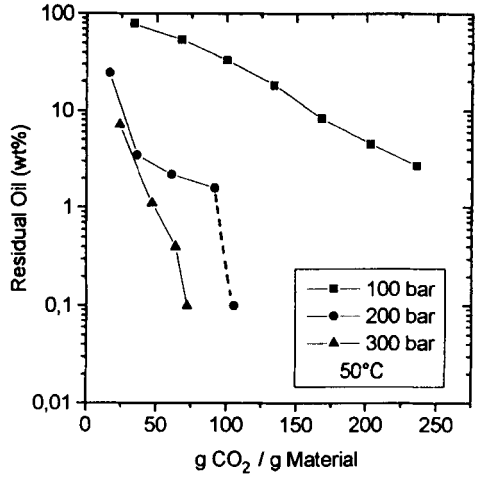

FIGURE 6. Residual oil content for different pressures

clearly reduced the oil content below 1%. This step is represented in Fig.6 by the dotted segment of the line. Extraction at 400 bar, on account of the stronger solvent power of supercritical CO_2, causes the oil residues to be leached out more quickly.

By coupling the static mode with the dynamic mode of operation, effective extractions can be accomplished even at high flow rates, which is evident from Fig.7. Here the oil contents of the sample have been plotted over the specific CO_2 throughput (g CO_2/g of material) for an extraction at 200 bar and at 50°C, once in the dynamic mode (flow rate 0.5 ml/min) and once in the static-dynamic mode (5 min stat.; 2 ml/min dyn.). The oil content of the sample decreases at a clearly faster rate in static-dynamic extraction than in the dynamic mode. After a throughput of only 30 g CO_2/g, a TOC value of <1% residual oil has certainly been attained, whereas in dynamic extraction the oil content of the sample is higher by more than one order of magnitude.

The static step extends the time of dissolution of the oil. This means that in the fluid phase a higher oil concentration is attained than during the short dwell time in the dynamic mode. The supercritical CO_2 phase, which is rich in oil, can then be flushed out of the extractor at a high flow rate. Altogether, the static-dynamic method thus allows a more effective extraction with clearly lower CO_2 consumption.

In order to determine optimum operating parameters for this coupled mode of operation, the FID of the Suprex equipment was used as on-line monitor. Continuous monitoring of the course of extraction, via measurement of the oil content of the fluid phase, allowed a relatively quick and safe statement to be made about the influence of the process variables, e.g., the holding times of static extraction and the flow rates of dynamic extraction (15).

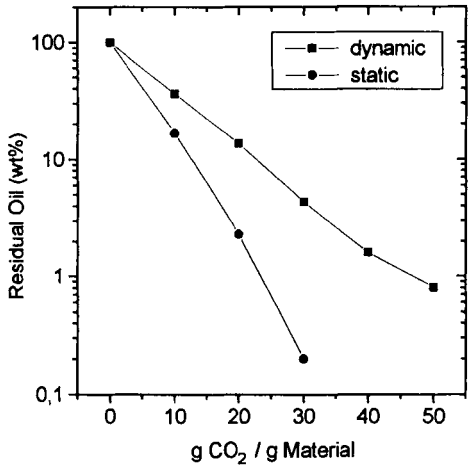

FIGURE 7. Residual oil content for a dynamic and a static extraction mode

The finalizing demonstration of the method was performed in the bench-scale plant described above (see Fig.1). About 3 kg each of grinds could be filled into the extractor insert (2.4-dm^3 volume). Two experiments were performed. The operating data have been entered in Table 1. After each extraction step the plant was stopped, the pressure relieved, and samples for TOC analyses were collected from various filling levels of the extractor. The TOC values and the extraction yields calculated from them are likewise entered in Table 1. The first batch was extracted stepwise at 200 and 300 bar with a total of 59 kg CO_2 and 19 g CO_2/g, respectively. In the second batch (static-dynamic mode at 200, 300 and 400 bar, 15-min holding times each), 45 kg CO_2 were used, which is equivalent to 15 g CO_2/g. In the remaining glass powder a residual content of 0.6% TOC was found, whereas the starting material contained 25.1% TOC.

The results of laboratory experiments on oil separation from glass grinds have been fully confirmed by the demonstration of the method in the

TABLE 1. RESULTS OF THE BENCH-SCALE PLANT

Pressure (bar)	Flow ($kg\ h^{-1}$)	Throughput (kg CO_2)	Specific throughput (g CO_2/ g material)	Extraction (%)	TOC (%)
	Experiment No.1, Input 3.18 kg, CO_2-flow upward				
200	7.6	28.4	8.9	14.6	11.3^u,7.7^l
200	stat. 15 min				
200	6.6	11.2	3.5	23.7	1.9^u,1.8^l
300	stat. 15 min				
300	13	19.2	6.0	28.9	0.5^u,0.6^l
	Experiment No.2, Input 3.03 kg, CO_2-flow downward				
200	stat. 15 min				
200	10.0	10.2	3.5		
300	stat. 15 min				
300	11.2	11.2	3.7		
400	stat. 15 min				
400	10.4	10.4	3.4	18.2	3.1^u,7.6^m, 16.9^l
300	stat. 15 min				
300	6.7	13.3	4.4	27.9	0.6^u,0.6^l

u = upper; m = middle; l = lower part of the extractor.

bench-scale plant; this is evident from the data in Table 1. The extractions in the bench-scale plant were performed in the static stage with holding times of 15 min. Dynamic extraction was accomplished with CO_2 mass flow rates of 8-13 kg/h, which corresponded to a specific mass flow rate of 1.7-2.8 g/cm^2min and a flow rate, respectively, of 2-4 ml/min. By transition from the laboratory-scale to the bench-scale plant, scaling up by the factor 2000 was successfully demonstrated.

As the method of oil separation by means of supercritical carbon dioxide is also excellently suited to treat metal grinds, the following further activities are planned in this context:

- the method based on a coupled mode of operation will be optimized in terms of extraction time and CO_2 consumed; and
- within the framework of a large experiment to be performed in a technical-scale extractor of 200:1 volume, a detailed cost calculation will be performed for this method.

ACKNOWLEDGMENTS

The authors thank Mrs. P. Kunz and Messrs. F. Becker, K. Buchmüller, P. Schwab, and H. Wilde for careful performance of the many experiments. They thank Dr. Boukis for determination of the particle size and Dr. Stieglitz and co-workers for the GC-MS analyses.

REFERENCES

1. N. Dahmen, J. Schön, H. Schmieder, K. Ebert, Supercritical fluid extraction of grinding and metal cutting waste contaminated with oil, presented at the ACS Spring National Meeting, New Orleans, LA, March 24.-28, 1996, to be published in ACS Symposium Series.

2. K.D. Bartle et. al., J. Phys. Chem. Ref. Data 20, 713 (1991).

3. G.M. Schneider, E. Stahl, G. Wilke, Eds., Extraction with Supercritical Gases, Verlag Chemie, Weinheim (1980).

4. E. Stahl, K.-W. Quirin, D. Gerrad, Verdichtete Gase zur Extraktion und Raffination, Springer Verlag, Heidelberg (1986).

5. M.B. King, T.R. Bott, Eds., Extraction of Natural Products using Near-Critical Solvents, Chapman and Hall, London (1993).

6. L.T. Taylor, Supercritical Fluid Extraction, John Wiley & Sons, Inc., (1996).

7. B. Wenclawiak, Ed., Analysis with Supercritical Fluids: Extraction and Chromatography, Springer Verlag, Heidelberg (1992).

8. G. Brunner, Gas Extraction, An Introduction to Fundamentals of Supercritical Fluids and the Application to Separation Processes, Steinkopff Darmstadt, Springer, New York (1994).

9. M.A. McHugh, V.J. Krukonis, Supercritical Fluid Extraction, Principles and Practice, Butterworth, Boston (1993).

10. F.R. Groves, B. Brady, F.C. Knopf, in Critical Reviews in Environmental Control, Vol. 15/3, C.P. Straub Ed., CRC Press, 1985, p. 237.

11. M. Modell, in Management of hazardous and toxic waste in the process industries, S.T. Kolaczkowski, B.D. Crittenden, Eds., Elsevier Applied Science, 1987, p. 67.

12. E. Kiran, J.M.H. Levelt Sengers, Eds., Supercritical Fluids, Fundamentals for Application, NATO ASI Series, Series E: Applied Sciences Vol. 237, Kluwer Academic Publishers, Dordrecht (1994).

13. U. Sievers, Thermodynamische Eigenschaften von Kohlendioxid, VDI-Fortschrittsberichte, Reihe 6, Nr. 155 (1984).

14. W.J. Schmitt, R.C. Reid, Chem. Eng. Comm. 64, 155 (1988).

15. J. Schön, N. Dahmen, FID-In-line monitor for the optimization of the SFE-Technique, 3. European Symposium on Analytical SFC and SFE, Uppsala, 6-8 September, 1995.

16. J. Tehrani, Successful Supercritical Fluid Extraction Strategies, American Laboratory, Feb. 1993, 40 HH-40 MM.