Characterisation and Process Development of Supercritical Fluid Extraction of Soybean Oil

M. Dobarganes Nodar, A. Molero Gómez* and E. Martínez de la Ossa

Department of Chemical Engineering, Food Technology and Environmental Technology, University of Cádiz, Apdo. 40, E-11510 Puerto Real, Cádiz, Spain

This work describes and analyses the extraction of soybean oil using supercritical carbon dioxide as a solvent from the point of view of both operative method and pre-treatment of the raw material. The best conditions for soybean oil extraction were obtained at a pressure of 300 bar, a temperature of 40 °C and a solvent flow rate of 1.8 L/min at STP. The yields obtained using the supercritical fluid under the best operating conditions were similar to those obtained by conventional extraction methods using hexane as the solvent (19.9 %w/w.); furthermore, the quality of oil extracted by the supercritical fluid was higher (acidity, 0.8). The fatty acid composition of the soybean seed oil extracted by supercritical fluid was particularly rich in unsaturated fatty acids, particularly linoleic acid (51.8%). For these reasons, the soybean seed oil extracted using supercritical carbon dioxide could compete with that obtained by the conventional process, since the oil refinement stages are simplified significantly and the solvent distillation stage is completely removed, which are the two most costly processing stages in terms of energy consumption.

Key Words: supercritical fluids, extraction, soybean oil, linoleic acid

INTRODUCTION

Supercritical fluid extraction (SFE), particularly involving the use of carbon dioxide, has been applied in numerous different fields. The decaffeination of coffee, production of hop flavours for use in beer making (Sthal et al., 1988; Bork and Körner, 1991), extraction of aromas and flavours (Bunzenberger et al., 1984; Raasch and Knorr, 1990), extraction of spices (Quirin and Gerard, 1990) and extraction and refining of edible oils (Sthal et al., 1980; Eggers, 1996) are some of the many industrial applications.

This separation technique offers extraction yields that are very similar to those obtained by conventional extraction processes using liquid solvents, but it requires a pre-determined combination of operating temperature and pressure. The advantages of this technique, compared to organic solvents used in the conventional extraction methods, are that carbon dioxide is non-toxic, non-flammable, non-corrosive and is also cheap and readily available in bulk quantities with a high degree of purity (Molero et al., 1996). Carbon dioxide also has a relatively low critical pressure and temperature (73.8 bar and 31.1 °C, respectively) and, as such, it can be considered as the perfect solvent to extract natural products, which require mild treatments to preserve the nutritive and sensory characteristics.

Traditionally, soybean oil has been obtained by a conventional extraction process using hexane as solvent. Nevertheless, after the extraction, a further stage is required to remove the solvent to levels below the minimum concentrations allowed by the relevant regulations that depend on the final destination of the product (Fernández, 1992; Domínguez et al., 1995). The application of SFE to obtain vegetable oils leads to a high quality product that can be used directly, thus precluding the removal and recovery of solvent by distillation.

It has been found in previous studies that the oil obtained from soybean with supercritical carbon dioxide ($SC–CO_2$) has some inherent advantages, including low phosphorus and iron contents due to the low solubility of phospholipids in $SC–CO_2$ (Cocero and Calvo, 1995). In addition, the colour of the oil obtained is lighter due to the low solubility in $SC–CO_2$ of carotenes and other pigments (Eshtiaghi et al., 1991).

The composition of soybeans is around 40% protein, 20% lipids, 17% cellulose and hemicellulose, 7% sugar, 5% crude fibre and 6% ash. The beans have a high oil content, at approximately 35–40% by weight, and this oil has a unique composition in comparison with most of the other common vegetable oils as well as having a higher content of linoleic acid. The fatty acid composition of soybean oil is somewhat different but, in other respects it is similar to other vegetable oils. It is a polyunsaturated oil and contains around 54% of linoleic acid (Fernández, 1992; Domínguez et al., 1995).

The work described in this paper involved the extraction of soybean oil using supercritical carbon dioxide as solvent. Working conditions for the process

**To whom correspondence should be sent (e-mail: andres.molero@uca.es).*
Received 21 March 2002; revised 10 October 2002.

Food Sci Tech Int 2002;8(6):0337–6

ISSN: 1082-0132
DOI: 10.1106/108201302031651

(operating pressure, temperature and solvent flow rate) and the pre-treatment of the raw material (grain size) were studied, and the fatty acid composition of the oil obtained under the best extraction conditions were determined.

MATERIAL AND METHODS

The soybean seeds (William's variety) used for the processes were supplied by the Instituto de la Grasa (Sevilla, Spain). The soybean seeds were crushed in a coffee mill of 2 kg capacity (Futurmatmodel FP, Barcelona, Spain) prior to extraction. Dehydration of the seeds was carried out by heating to 65 °C until constant weight was achieved. The equipment used for the SFE processes with carbon dioxide was the SCE screening system model manufactured by Autoclave Engineers (Erie, PA, USA). A schematic diagram of this equipment is shown in Figure 1.

Liquid CO_2 was cooled to prevent its gasification and introduced into an HPLC pump of 46–460 mL/h capacity and fitted with a cooled head. The extraction vessel was a 316 SS high pressure cylinder (40 mL volume) that was capable of operating up to 400 bar and 340 °C. The vessel was fitted with an electrical heating jacket. A sample (about 20 g) was placed in the extractor vessel. The pressure of the CO_2 cylinder was maintained throughout the system by opening valves V-1 and V-2 and closing the valve V-3. Before the pump was switched on, the valves V-1 and V-2 were closed. The pump was then switched on and its output pressure increased using the pressure regulating valve until the required processing pressure was reached. The compressed CO_2 was subsequently introduced into the extractor vessel by opening valves V-1 and V-2. When the desired pressure was attained, the heating jacket was switched on to give the required operating temperature. When both the desired pressure and temperature had been reached, the extraction was started by opening valve V-3. The flow rate of carbon dioxide through the extractor vessel was regulated by the flow micrometer valve. The oil dissolved in the supercritical CO_2 was separated from the carbon dioxide and collected in the separator (100 mL capacity, 316 SS) at ambient temperature and pressure. The CO_2 was passed through an in-line volumetric flow meter, which controlled the quantity and flow rate of CO_2 used. The flow meter used was a model FC-70 supplied by EG&G Flow Technology (Phoenix, AZ, USA).

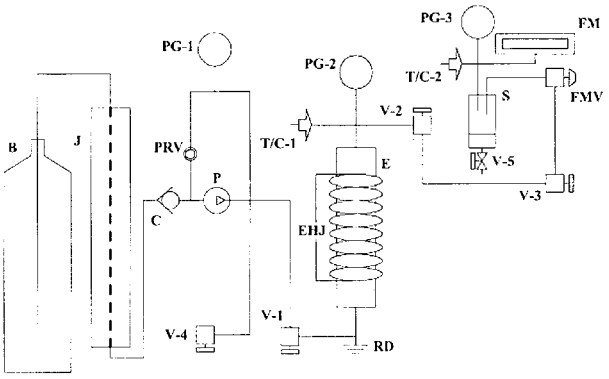

Figure 1. Schematic diagram of supercritical CO_2 extraction apparatus: B, liquid CO_2 cylinder; J; cooler, C, check valve; P, pump; PRV, pressure regulating valve; E, extraction vessel; S, separator; EHJ, electrical heating jacket; RD, rupture disk; FMV, flow micrometric valve; T/C-1,2, thermocouples; V-1 to 5, shut-off valves; PG-1 to 3, pressure gauges and FM, flowmeter.

In order to compare the SFE method studied here with the conventional extraction process using liquid solvents, the use of a "Soxhlet"-type apparatus with hexane as solvent (250 mL of hexane and 30 g of soybean seed) was also studied. The extraction time was 16 h, which guaranteed full depletion of the seed and allowed the maximum possible extractive yield to be determined. These values are considered very important to establish a sound basis for direct comparison to the SFE process.

The amount of oil obtained by the two extraction techniques was determined gravimetrically. In all cases, the yield of the extraction has been expressed as the grams of oil extracted per grams of soybean seeds.

The extraction process was carried out within the following ranges of operating conditions: pressure, from 100 to 380 bar; temperature, 40 and 60 °C; solvent flow rate, 0.8 and 1.8 L/min at STP.

The physico-chemical characterisation of the extracted oils was performed according to the indexes for the analysis of oils for human consumption (AOCS, 1983). The indexes determined were acidity (% of oleic acid), iodine (Hanus method), saponification and peroxides.

The fatty acid composition of the oil was determined, after methylation, by gas chromatography using a model 5890 Hewlett Packard chromatograph (Pittsburgh, PA, USA) fitted with a Carbowax 20M (Supelco, Bellefonte, PA, USA) capillary column and an FID detector.

All the products and chemical reagents used were of analytical quality. The carbon dioxide used was of 99.95% purity from Carburos Metálicos, S. A. (Sevilla, Spain).

RESULTS AND DISCUSSION

Extraction of Soybean Oil with Supercritical Carbon Dioxide

The yield of soybean oil obtained with supercritical CO_2 increased with extraction pressure for both temperatures (Figure 2). Furthermore, at pressures

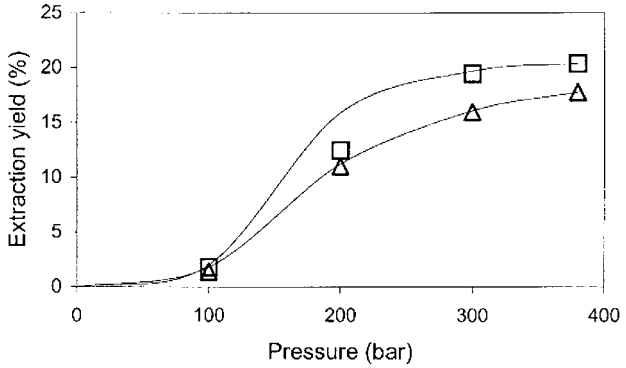

Figure 2. Effect of pressure on extraction yield of soybean oil using supercritical carbon dioxide at two different temperatures (extraction time 8 h; STP solvent flow rate, 1.8 L/min; soybean seed size, 0.3 mm). (□) 40°C, (△) 60°C.

above 250 bar, high increments in pressure produce only a small increment in the yield.

The differences in yield for the extraction of different oils can be explained in terms of the nature of the seeds (Sthal et al., 1980; Molero et al., 1996). For example, an appropriate combination of pressure and temperature is needed to obtain the best solvent capacity for the CO_2 (which is closely related with the density) in the extraction, in which the solvent must be able to penetrate and overcome the mass transfer resistance to extract the oil from the seed.

On the other hand, temperature was found to have a relevant influence on the yield of the extraction process. At 60 °C, a pressure of 380 bar was needed to reach a similar yield to that obtained at 250 bar and 40 °C.

The amount of soybean oil extracted per unit of carbon dioxide depended on the flow rate of solvent (Figure 3). The flow rate used in the extraction process is important because the residence time in the extractor increases as the flow rate decreases. The lower the flow rates the better the solubility equilibrium is maintained in the later stages of the extraction (Friedrich and List, 1982).

Higher flow rates lead to a larger quantity of oil, but this is also associated with a higher solvent consumption. Lower flow rates require smaller amounts of solvent, but the process time is longer to obtain the same extraction yield. The maximum extraction yield was obtained at solvent flow rates of around 1.8 L/min at STP.

When these data are plotted against the extraction time (Figure 4) the lower solvent flow rate needed more extraction time to achieve a satisfactory extraction yield. For the solvent flow rate of 1.8 L/min, the extraction time was 5 h.

The quantity of oil extracted increased as the particle size decreased (Figure 5). It is reasonable to suppose that the oil is localised in the interior of the seed and, in this case, the internal mass transfer resistance is lower when the seed is crushed.

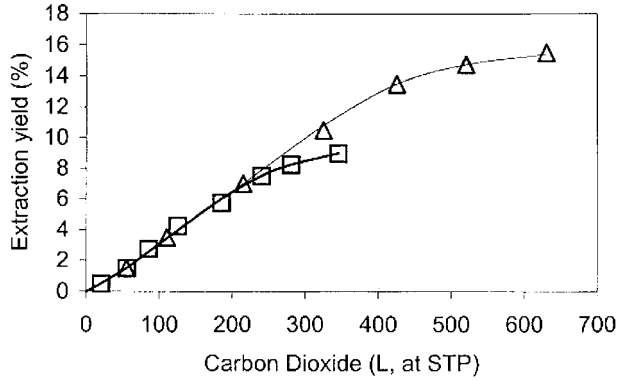

Figure 3. Effect of supercritical carbon dioxide flow rate on extraction yield of soybean oil (pressure, 200 bar; temperature, 40°C; soybean seed size, 0.3 mm). (□) 0.8 L/min, (△) 1.8 L/min.

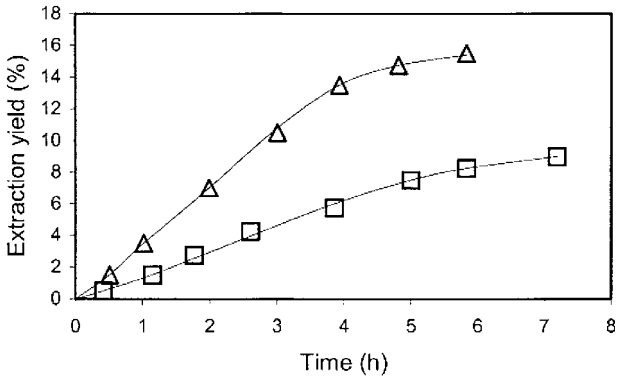

Figure 4. Effect of extraction time on extraction yield of soybean oil by supercritical carbon dioxide (pressure, 200 bar; temperature, 40°C; soybean seed size, 0.3 mm). (□) 0.8 L/min, (△) 1.8 L/min.

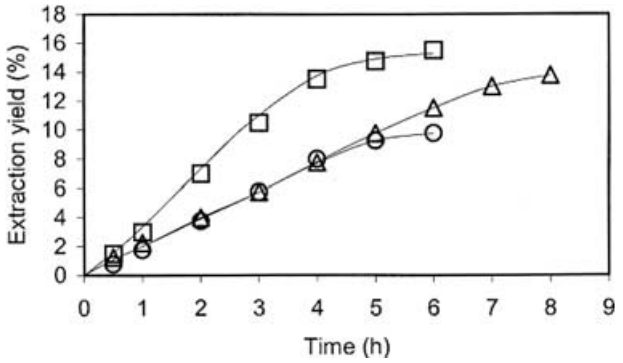

Figure 5. Effect of particle size on extraction yield of soybean oil (pressure, 380 bar; temperature, 40°C; STP solvent flow rate, 1.8 L/min). (□) 0.30 mm; (△) 0.75 mm; (○) 1.00 mm.

The maximum yield obtained for the particles with the biggest size (1 mm) was 9.73%, which represented almost 6% less than the yields obtained for particles of 0.3 mm. This reduction in yield is a result of the change in the internal mass transfer resistance. From the results obtained for the three particle sizes studied, it seems

clear that the resistance to internal mass transfer will decrease as particle size decreases. For particle sizes larger than 0.3 mm, a higher extraction time is needed to reach the same yields as those obtained with smaller particle sizes.

A similar effect was observed in previous studies, which confirmed that the seeds have to be crushed to ensure a satisfactory extraction yield (Molero et al., 1996). However, wheat germ oil does not need pretreatment prior its extraction (Taniguchi et al., 1986; Molero and Martínez, 2000).

On the basis of the above discussion, the best yields for the extraction of soybean oil by supercritical carbon dioxide are obtained at a pressure of 300 bar, a temperature of 40 °C, a solvent flow rate of 1.8 L/min (at STP) and a milled seed size of 0.3 mm. Under these conditions the extraction time was 5 h.

Comparison of SFE Versus Other References

Extraction Yields

The data in Table 1 provide a comparison of the SFE and conventional hexane extraction yields from soybean seeds in this study with the results obtained by other authors. Those data show that pressures greater than 200 bar are required in order to obtain a good yield in the process. The yields obtained were, in all cases, lower than those obtained using the conventional solvent extraction technique with hexane as a solvent.

The fact that the SC–CO_2 has a high selectivity is well known (Taniguchi et al., 1986; Zhao et al., 1987; Molero and Martínez, 2000) and it is of interest to analyse the differences between the oils extracted using the two methods. Only by establishing the differences between the extracted compounds can the use of a new method of extraction be justified. The soybean oil extracted by SFE using carbon dioxide is solvent free. For this reason, the distillation process usually required to recover the solvent is not needed.

Oil Composition

Comparison of the results obtained in this work is not straightforward due to the fact that only a few references on this subject are available in the literature. For this reason, the comparison of some relevant parameters for other vegetable oils extracted with supercritical carbon dioxide (Table 2) in order to establish a better comparison of the quality of the soybean oil obtained in this study is interesting.

The free fatty acid and peroxide indexes are the most important parameters to evaluate the degree of oil degradation. The first of these values provides information about the hydrolytic deterioration that may have occurred in the oil; and, the peroxide index approaches the extent to which certain components of the oil have suffered oxidation (tocopherols and polyphenols). As one would expect, low values for these indexes indicate that oil degradation is minimal.

The values obtained for the soybean oil extracted by CO_2 supercritical was very low in comparison with the other vegetables oils shown in Table 2. Only the acidity of grape seed oil is close to the value in this work for the soybean oil. Furthermore, the value for the free fatty acids is very close to that permitted for human consumption. This particular aspect is very important because the subsequent neutralisation stage in the refining process must be applied on a small scale.

The higher values obtained for the saponifiable matter and the low values for the free fatty acids, indicated that that the soybean oil extracted by supercritical CO_2 had a high triglyceride content. This high content is only exceeded by the grape seed oil. In addition, the iodine index also has a high value due to the higher percentage of unsaturated fatty acids present in the oil (Table 2).

Table 1. Comparison of soybean oil extraction yields using supercritical carbon dioxide and hexane as solvents.

	Yield (wt.%)	
Soybean	SFE Using CO_2	Extraction Using Hexane
This work (300 bar, 40°C)	19.5	25.0
Sthal et al., 1980 (300 bar, 40°C)	16.4	19.9
Friedrich and List, 1982 (350 bar, 50°C)	19.9	20.0

Table 2. Physico-chemical characterisation of vegetables oils extracted using supercritical carbon dioxide.

Oil	Saponification Value	Iodine Value (Hanus)	Free Fatty Acids (% Oleic)	Peroxide Value (meq O_2/kg oil)
Soybean (this work) (300 bar, 40°C)	194	127	0.8	7.2
Grape seed (Molero et al., 1996) (350 bar, 40°C)	259	98	3.4	383.0
Soybean (Friedrich and List, 1982) (350 bar, 50°C)			0.5	<0.1
Wheat germ (Molero and Martínez, 2000) (150 bar, 40°C)	185	102	14.0	75.0
Borage seed (Molero and Martínez, 2001) (300 bar, 40°C)	163	198	11.0	33.5
Soybean (FAO, 2001)	189–195	124–139	0.6	<10.0

Table 3. Percentage of fatty acids of soybean oil extracted by supercritical carbon dioxide.

Soybean	C16:0 (Palmitic)	C16:1 (Palmitoleic)	C18:0 (Stearic)	C18:1 (Oleic)	C18:2 (Linoleic)	C18:3 (Linolenic)
This work (300 bar, 40 °C)	11.8	0.2	4.2	23.7	51.8	6.5
Friedrich and List, 1982 (350 bar, 50 °C)	11.0		3.5	27.5	52.0	6.0
Soybean (FAO, 2001)	5.0–7.6	<0.3	2.7–6.5	14.0–39.4	48.3–74.0	<0.3

In summary, the quality of soybean oil obtained using supercritical CO_2 is similar to that of oil refined and extracted with an organic solvent, consequently the refining process may be used on a small scale.

Fatty Acid Composition

Fatty acid composition of the soybean oil obtained using supercritical CO_2 as solvent were compared with those obtained by Friedrich and List and the values regulated for human consumption (Table 3). The content in fatty acids is very similar in both studies. When these values are compared with those given by FAO, it can be seen that they are within the established limits. This aspect is of vital importance in terms of the subsequent refining process.

The high content in unsaturated fatty acids (82%) and the lower proportion of saturated fatty acids (12%) justifies the above discussion regarding the values of the physico-chemical indexes and makes it particularly appropriate to consider using such oil in the alimentary industry.

Therefore, despite the high costs of the process plant, SFE could prove to be more economical than conventional organic extraction. However, further studies regarding costs are needed to confirm these latter conclusions.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to the Instituto de la Grasa (Sevilla, Spain) for valuable discussions, help in obtaining technical data, and for providing the material required for the experiments.

REFERENCES

AOCS (1983). *Official and Tentative Methods of the American Oil Chemists Society*. 3rd Edn. Illinois: AOCS.

Bork M. and Körner J.P. (1991). Extraction by use of supercritical solvents. *ZFL, -Internationale Zeitschrift fuer Lebensmittel Technik, Marketing, Verpackung und Analytik* **42**(12): 732–738.

Bunzenberger G., Lack E. and Marr R. (1984). CO_2-extraction: comparison of super and subcritical extraction. *German Chemistry and Engineering* **7**: 25–31.

Cocero M.J. and Calvo L. (1995). Planta piloto-laboratorio de extracción con CO_2 supercrítico para la obtención de aceites de semillas. *Alimentación, Equipos y Tecnología* **14**(3): 67–75.

Domínguez H., Sineiro J., Núñez M.J. and Lema J.M. (1995). Incorporación de un tratamiento enzimático para mejorar la extractabilidad del aceite de semillas en distintos procesos. *Alimentación, Equipos y Tecnología* **14**(3): 59–66.

Eggers R. (1996). Supercritical fluid extraction of oilseeds/lipids in natural products. In: King J.W. and List G.R. (eds), *Supercritical Fluid Technology in Oil and Lipid Chemistry*. Illinois: AOCS Press.

Eshtiaghi M., Messerschmidt K. and Knorr D. (1991). Supercritical fluid extraction of pigments from peels of orange fruits. *ZFL, -Internationale Zeitschrift fuer Lebensmittel Technik, Marketing, Verpackung und Analytik* **42**(11): 61–64.

FAO (2001). *The Codex Alimentarius*. Vol. 8. Rome: FAO.

Fernández P.M. (1992). Aceites y grasas vegetales comestibles. Definiciones, disposiciones legales y aspectos nutricionales. control de calidad y pruebas de pureza (i). *Alimentación, Equipos y Tecnología* **11**(3): 47–55.

Friedrich J.P. and List G.R. (1982). Characterization of soybean oil extracted by supercritical carbon dioxide and hexane. *Journal of Agricultural and Food Chemistry* **30**: 192–193.

Molero Gómez A., Pereyra López C. and Martínez de la Ossa E. (1996). Recovery of grape seed oil by liquid and supercritical carbon dioxide: a comparison with conventional solvent extraction. *The Chemical Engineering Journal* **61**: 227–231.

Molero Gómez A. and Martínez de la Ossa E. (2000). Quality of wheat germ oil extracted by liquid and supercritical carbon dioxide. *Journal of the American Oil Chemists' Society* **77**(9): 969–974.

Molero Gómez A. and Martínez de la Ossa E. (2001). Quality of borage seed oil extracted by liquid and supercritical carbon dioxide. *The Chemical Engineering Journal* **86**: 1–7.

Quirin K.W. and Gerard D. (1990). High pressure extraction of spices. *ZFL, -Internationale Zeitschrift fuer Lebensmittel Technik, Marketing, Verpackung und Analytik* **41**(11): 731–734.

Raasch A. and Knorr D. (1990). Supercritical-fluid-extraction of flavours compounds from peels of passion fruits. *ZFL, -Internationale Zeitschrift fuer Lebensmittel Technik, Marketing, Verpackung und Analytik* **41**(3): 8–12.

Stahl E., Schütz E. and Mangold H.K. (1980). Extraction of seed oils with liquid and supercritical carbon dioxide. *Journal of Agricultural and Food Chemistry* **28**: 1153–1157.

Stahl E., Quirin K.W. and Gerard D. (1988). *Dense Gases for Extraction and Refining*. New York: Springer Verlag.

Taniguchi M., Tsuji T., Shibata M. and Kobayashi T. (1986). Extraction of oils from wheat germ with supercritical carbon dioxide. *Agricultural and Biological Chemistry* **49**(8): 2367–2372.

Zhao W., Shisshikura A., Fujimoto K., Arai K. and Saito S. (1987). Fractional extraction of rice bran oil with supercritical carbon dioxide. *Agricultural and Biological Chemistry* **51**(7): 1773–1777.