Extraction of lipids from oleaginous seeds with supercritical CO_2: Process parameters and products content

Olivier Boutin*, Elisabeth Badens

Université Paul Cézanne Aix-Marseille

UMR-CNRS 6181 M2P2, Mécanique, Modélisation et Procédés Propres

Europôle de l'Arbois BP 80 13545 Aix en Provence Cedex 4 France

* Corresponding author: Phone number: (+ 33) 442 90 85 12

Fax number: (+ 33) 442 90 85 15

e-mail: olivier.boutin@univ-cezanne.fr

Abstract

In the field of extraction processes, using supercritical fluids such as CO2 overcomes many drawbacks linked to the use of liquid organic solvents such as liquid hexane. In order to study the influence of different parameters on the oil extraction yield for two types of seeds (rape and sunflower) using supercritical CO2, an experimental design is built: pressure (15 - 45 MPa), temperature (35 - 75 °C), CO2 flow rate (8 - 19 $kg.h^{-1}$) and extraction duration (20 - 120 min). Extraction yields are between 0.3 to 89.8 %, indicating that the experimental design covers a large range of results. The experimental design results allow obtaining a polynomial representing the evolution of this yield with the four entry parameters. These results indicate that the evolutions are, for a part, different for the two seeds. For rape seeds, the main parameter influencing the extraction yield is pressure while temperature has a small influence. Concerning the obtained results on sunflower seeds, pressure and temperature have a significant influence. At lower pressure, it is necessary to work at 75 °C to have an interesting extraction yield. At higher pressure, it is possible to work at different temperatures, even if this parameter has still an influence. Besides, for the same operating conditions, the extraction

yields for sunflower seeds are lower than for rape seeds. Thermodynamic effects (solubility) and kinetic effects (mass transfer depending on the seeds) have been evidenced. Several analyses have also been done: acidic and phosphorus content in the oil, protein content in the residual cake. The selectivity of pure supercritical CO2 has been shown: any phospholipid is extracted. In addition to selectivity, another interest of the process is the purity of the products recovered, totally free from organic solvent.

Introduction

Using supercritical fluids such as CO2 for extraction processes overcomes many drawbacks (mainly toxicity and storage security) linked to the use of liquid organic solvents such as liquid hexane. Indeed, supercritical CO2 is non toxic, no flammable and separation from a solid or a liquid is easily done by a simple depressurization. There is no residual organic solvent traces in the final products which is very important for agro food applications. Moreover, CO2 critical temperature is low (31 °C), which is interesting for the extraction of thermolabile components. By varying pressure beyond its critical value (7.38 MPa), it is possible to vary the selectivity of the extraction. Eventually, the physical properties of supercritical CO2 (viscosity and mass transfer coefficient) allows a good penetrability of the solvent in the solid matrix. Oils from these seeds are composed of many lipids, mainly triglycerides and minor lipids which are usually unsaponifiable: vitamins, sterols, pigments and phospholipids (Güçlü-Üstündag and Temelli, 2004). Before any extraction, seeds are usually pretreated in order the facilitate further solvent extraction (del Vallé *et al.*, 2006). Frequently, the first pre-treatment consists of a cold pressing by a simple mechanical action. However, this pretreatment is non selective as all lipids are extracted at the same time. Other pre-treatments are also possible preparing the seeds for further extraction but they do not extract any oil (Fattori *et al.*, 1988): flaking, cooking, crushing, grinding and chopping.

In this work, the extraction using supercritical CO2 is studied on two seeds: sunflower and rape seeds. For each one, the qualitative and quantitative influences of several parameters on the obtained products are studied.

Material and methods

Seeds are first pretreated using the flaking process (the size of the system is adjusted, depending on the size of the untreated seeds: 0.1 mm for rape seeds and 0.35 mm for sunflower seeds). The seeds are then dried with hot air (70-80°C) during four hours. The extractor (Separex, France) set up is presented on Figure 1. Its main characteristics are the following: 12.5 cm diameter, 24 cm height, 3 L volume, 30 µm porosity frit filters at the exit.

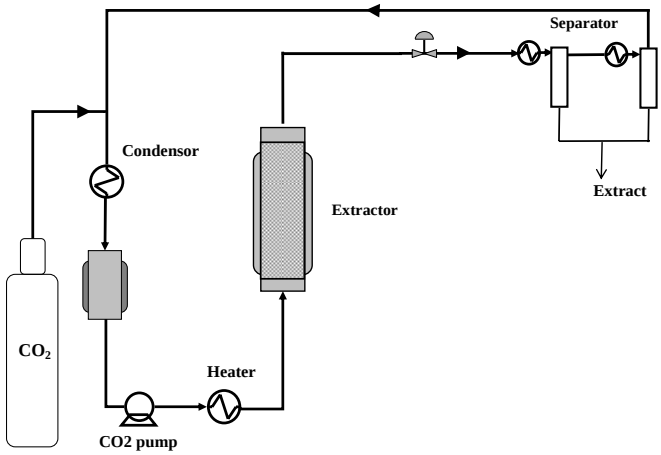

Figure 1 Extraction experimental set-up

The experimental procedure for the extraction is very common and will not be detailed in this short communication (see for instance Eggers, 1996). The CO2 used during the extraction was provided by Air Liquid (France). The initial load is 1 kg of pre-treated seeds. The seeds global composition before extraction is:

- Initial lipids content: 36.9 g for 100 g of pre-treated rape seeds.
- Initial proteins content: 22.2 g for 100 g of pre-treated rape seeds.
- Initial lipids content: 45.1 g for 100 g of pre-treated sunflower seeds.
- Initial proteins content: 19.2 g for 100 g of pre-treated sunflower seeds.

Analyses have been carried out on the seeds and on the recovered oil. Lipids are analysed using NF V 18-117 and EC Dir 98/64 standards (minimal quantity for an analysis is 100 g; results given in g of lipids for 100 g of seeds).The raw proteins is measured using the Kjeldahl combustion method (MO575) (minimal quantity for an analysis is 100 g; results given in g of

lipids in 100 g of seeds). The acid content in the oil is determined using standard ISO 660:1996 which is a titrimetric measurement. The results are given in KOH mg per oil g. The phosphorus content is then determined using ICP (Inductively Coupled Plasma) or AAS (Atomic Absorption Spectroscopy). The results are given in phosphorus mg per oil kg (ppm). The detection limit of the apparatus is 3 ppm.

An experimental design allows studying the influence of several operating parameters (pressure, temperature, time of extraction, CO2 flowrate). In this work, the response is the extraction yield, defined as the ratio between the oil recovered during the extraction upon the oil initially contained in the virgin seeds. This last quantity is determined by the lipids analysis on pre-treated seeds. The statistical analysis is common and usual and will not developed in this paper (see for instance Kiriamati *et al*., 2002). It was based on the NEMRODW software (2000-D, LPRAI Corporation, France). The 27 experiments to be conducted are given in Table 1, with three replicates at the centre of the design.

Experimental results

All the results obtained for seeds extraction are given in Table 2. The results covered a large field of values, with extraction yields from 0.3 to 89.8 wt %, indicating that the different experimental domains have been hence carefully chosen. The variance analysis indicates that the model is significant (sig.<0.001) at 99 % confidence. Concerning rape seeds extraction, the statistical results show that the main effects of pressure (sig. < 0.001), extraction duration (sig. < 0.001) and flow rate (sig. < 0.05) are significant to the extraction yield. Four interaction effects, pressure-temperature or time or flowrate and time-flowrate (sig. < 0.05), are also significant. Among the operating parameters, pressure plays a major role, far more than temperature, as its coefficient is ten times higher. Concerning the extraction of sunflowers seeds, the extraction is more difficult, probably due to higher mass transfer resistances (mainly internal since its external mass transfer is roughly the same in the two cases). When designing an extraction system, two aspects have thus to be considered: the thermodynamic aspects (with solubility) and the kinetics aspects (with mass transfers). The statistical results show that the main effects of pressure (sig.<0.001), extraction duration (sig.<0.001) and flow rate (sig.<0.05) are significant to the extraction yield, which are the same results as for rape seeds. Pressure is the parameter that influences more the extraction yield. In that case, the influence of temperature is more important than for rape seeds

extraction. Indeed, there is a factor 4 between the coefficients for pressure and temperature, in the case of sunflower, compared to the factor 10 previously mentioned for rape seeds.

Table 2 Experimental design conditions and yield results

Experimental design conditions					Rape seeds		Sunflower seeds	
Run	**Pressure (MPa)**	**Temperature (°C)**	**Time (min)**	**CO2 flowrate ($kg.h^{-1}$)**	**Oil/CO2 ($g.kg^{-1}$)**	**Oil recovery (wt %)**	**Oil/CO2 ($g.kg^{-1}$)**	**Oil recovery (wt %)**
1	15	35	20	8	1.4	1.1	4.0	2.4
5	15	35	120	8	1.9	8.0	2.3	8.2
3	15	75	20	8	0.6	0.5	0.9	0.5
7	15	75	120	8	0.3	1.3	0.3	1.1
9	15	35	20	19	0.9	1.5	0.9	1.3
13	15	35	120	19	1.8	18.8	1.4	11.6
11	15	75	20	19	0.4	0.6	0.2	0.3
15	15	75	120	19	0.2	2.0	0.1	1.2
17	15	55	70	13.5	0.9	3.7	1.2	4.0
2	45	35	20	8	4.4	3.2	3.7	2.2
6	45	35	120	8	10.4	45.0	6.4	22.8
4	45	75	20	8	8.6	6.3	8.8	5.3
8	45	75	120	8	14.4	62.4	16.3	57.8
10	45	35	20	19	4.7	8.0	1.4	2.0
14	45	35	120	19	7.1	73.1	5.5	46.1
12	45	75	20	19	8.1	13.8	9.5	13.3
16	45	75	120	19	8.7	89.8	9.3	78.5
18	45	55	70	13.5	11.0	45.5	12.7	42.9
19	30	35	70	13.5	3.4	14.1	5.0	16.7
20	30	75	70	13.5	6.6	27.4	3.2	10.6
21	30	55	20	13.5	2.2	2.5	4.6	4.3
22	30	55	120	13.5	3.6	15.0	4.4	14.8
25	30	55	70	13.5	5.6	39.6	6.0	34.7
26	30	55	70	13.5	4.1	17.0	5.3	17.8
27	30	55	70	13.5	5.6	23.0	6.1	20.7
23	30	55	70	8	6.1	15.5	3.4	6.9
24	30	55	70	19	3.0	18.2	3.4	32.6

The analysis results indicate that acidic concentration decreases with the increase of CO2 quantity. This is because the extraction of the acids takes place at the beginning of the extraction, leading to a decrease of their concentration with time. Concerning phosphorus content, no traces have been detected. It indicates that pure supercritical CO2 does not extract phospholipids and other minor lipids. This result is interesting as it allows extracting pure oil for food applications. The protein content in the solid residue normally increases while the quantity of oil extracted increases, till reaching the maximum value of 35 g for 100 g of residual cake. Those cakes do not contain any traces of residual organic solvent and for instance can be directly used for animal food.

Conclusion

An experimental design has been constructed in order to study the influence of the different parameters (pressure, temperature, time, CO2 flowrate) on the oil extraction yield. Several analyses have also been done: acidic and phosphorus content in the oil, protein content in the residual cake. For rape seeds, we demonstrated that the main parameter influencing the extraction yield is pressure while temperature has a small influence. On the contrary, concerning the results on sunflower seeds, pressure and temperature have a significant influence. Besides, for the same operating conditions, the extraction yields for sunflower seeds are lower than for rape seeds indicating that the mass transfer is more difficult in the seeds from sunflower than from rapeseeds. No phospholipids have been detected in the extracted oil showing that as expected the extraction with supercritical CO2 is selective. In that case, no oil degumming or oil refinery is necessary after this process.

References

Güçlü-Üstündag, Ö., Temelli, F. (2004). Correlating the solubility behavior of minor lipid components in supercritical carbon dioxide. *Journal of Supercritical Fluids*, 31, 235-253.

Eggers, R. (1996). Supercritical fluid extraction of oilseeds/lipids in natural products. In J.W. King, G.R. List (Eds), *Supercritical Fluid Technology in Oil and Lipid Chemistry* (pp.35-45).

Fattori, M., Bulley, N.R., Meisen, A. (1988). Carbon dioxide extraction of canola seed: oil solubility and effect of seed treatment. *Journal of American Oil Chemical Society*, 65, 968-974.

Kiriamiti, H.K., Rascol, E., Marty A., Condoret, J.S. (2002). Extraction rates of oil from high oleic sunflower seeds with supercritical carbon dioxide. *Chemical Engineering and Processing*, 41 (8) 711-718.

del Vallé, J., Germain, J.C., Uquiche, E., Zetzl, C., Brunner, G. (2006). Microstructural effects on internal mass transfer of lipids in prepressed and flaked vegetable substrate. *Journal of Supercritical Fluids*, 37 (2) 178-190.