

EXTRACTION OF ROSA MOSQUETA (*Rosa Aff. Rubiginosa*) OIL WITH DENSE FLUIDS

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Keywords: *Rosa Aff. Rubiginosa*, oil, near-critical extraction, thermodynamic modelling

Abstract

The use of compressed or liquefied gases as solvents, in extraction and fractionation processes, presents a potential application in pharmaceutical and food industries. Similarly to traditional liquid solvents, non-toxic gases such as carbon dioxide, applied at quasi-critical conditions, are able to dissolve non-volatile substances at relatively low temperatures. Their volatility facilitates its later elimination from the extract, leaving a final product with a very low level of residual solvent.

In this study, the solubility of rosa mosqueta oil in super-critical carbon dioxide was determined, at temperatures between 40° and 60°C and pressures in the range of 70 to 100 bar. The effects of pressure and temperature on the solubility behaviour have been evaluated, and the changes in phase miscibilities observed, in order to analyse the viability of a continuous or batch process to obtain oil from oil-seeds.

The results of high-pressure extractions with carbon dioxide and propane, are compared with the traditional, low-pressure extraction process with hexane, on the basis of the yield and quality of the extract, and the solubility of the oil in the solvents.

1. Introduction

Rosa mosqueta (*Rosa Aff Rubiginosa*) is a wild rose known in Europe as rose hip. In South America it grows in the Andes region of Argentina and Chile, where it is known as rosa mosqueta. It presents an invader behaviour, and it is difficult to eradicate. The animals eat their fruits, contributing to the dissemination of the species. It grows as a bush 2 meters high (Parodi, 1972).

The fruit (18% pulp, 2% shell, 33% seed and 47% water) is red in colour and it contains between 15 and 40 oval seeds, 2-3 mm of thickness, which yield about 6-7 wt% of oil on a dry basis. The oil extracted from these seeds is a mixture of triglycerides of fatty acids, with an approximate proportion of 5% saturated, 16% mono-unsaturated and 79% poly-unsaturated (41% linoleic, 39% linolenic) acids.

The rosa mosqueta oil has a cosmetological application in the elaboration of cream bases, solar screens, soaps and shampoos. It is also used in the treatment of skin burns, acne, warts and scars and it has proven to have restorative action on the epidermis.

2. Near-critical fluids

The rosa mosqueta oil is obtained from the seeds of *Rosa Aff Rubiginosa*, using the traditional cold pressing process and solvent extraction with hexane. It is of interest to explore the use of an alternative technology, efficient from the point of view of energy consumption, and which will avoid the use of pollutant fluids, harmful to the human health. In particular, special attention has been given to the application of innocuous

dense fluids, such as carbon dioxide or its mixtures with substances used as co-solvents, at near-critical conditions (Brunner, 1994; King and Bott, 1993; King and List, 1996).

Near-critical fluids are used as separation agents at a reduced temperature (ratio between process temperature and critical temperature of the fluid) between 0.9 and 1.3. They present high compressibilities, which result in important changes in density with moderate changes in pressure and/or temperature. This gives rise to solvent or antisolvent effects, depending on the process operating conditions. They also present some advantages regarding their transport properties, when compared to liquid solvents: lower values of viscosity and surface tension and higher diffusion coefficients; they have good permeation into solid cellular matrices, such as those involved in the extraction of oil from oil-bearing plant material.

One of the main advantages of supercritical extraction, is the fact that this process can be carried out at nearly ambient temperatures, making it attractive for processing thermally unstable compounds. On the other hand, the wide variation of density with temperature and pressure in the near-critical region, gives rise to important changes in the thermodynamic properties and phase behaviour of solute - supercritical solvent mixtures; this, in turn, enlarges the range of working conditions to carry out the extraction, fractionation and solvent recovery stages.

3. Phase equilibria thermodynamics

A good knowledge of the phase equilibrium behaviour of rosa mosqueta oil - solvent mixtures is needed in order to evaluate the performance of extraction and purification processes, either by traditional or supercritical technologies.

Typically, the mixtures of vegetable oils with low molecular weight solvents exhibit negative deviations to Raoult's Law at low solvent concentrations, and positive deviations in the solvent-rich area. Above a certain temperature (i.e. the lower critical temperature) a region of partial liquid miscibility is reached, giving rise to a liquid phase split at high solvent concentrations (de la Fuente, 1994) (see Figure 1).

This behaviour is mainly determined by the differences in the molecular size of the mixture components, rather than by their intermolecular potential energy. This is to be expected, taking into account the non-polar characteristic of the mixture, and the big differences between the molecular weight of the vegetable oils (about 800 to 900) and that of the solvents (between 40 and 90).

The use of classical van der Waal type of equations of state for modelling this phase behaviour, present two main drawbacks (de la Fuente *et al.*, 1997):

1. Pure component properties (critical properties and acentric factor) of the vegetable oils are experimentally unattainable, due to their extremely low vapour pressure and their thermal instability. These properties have to be estimated, generally by means of group contribution methods (Reid *et al.*, 1987). Care has to be taken with the values of the estimated properties, to avoid meaningless results from the equations, such as the prediction of negative vapour pressures.
2. Binary interaction coefficients have to be included in the mixing rules of both equation parameters: the co-volume and the energy parameter. The values of these interaction coefficients are obtained by fitting binary phase equilibrium data. However, two different sets of parameters are needed to correlate vapour-liquid equilibrium conditions on one hand, and liquid-liquid equilibria on the other.

The prediction of phase equilibria by means of group contribution methods appears as an interesting alternative: only three functional groups (paraffinic, olefinic and ester) can in principle represent all types of triglycerides present in vegetable oils. In this work, the

Group Contribution Equation of State (GC-EOS) (Skjold-Jorgensen, 1988) has been successfully applied in the calculation of high pressure phase equilibria of vegetable oils (Bottini *et al.*, 1998) (see Figure 1). Here, the parameter characterising the molecular size of the oil, can be obtained from experimental data on infinite dilution activity coefficients (Din *et al.*, 1995).

4. Pilot plant experiments

Two types of experiments were carried out: batch extractions in a 3.5 litres, high pressure Soxhlet extractor, and continuous extractions in a flow type unit of 250 cc capacity. The first type of experiments is useful to study extraction yields and solvent capacities. The second one allows to study the solubilities of the oil in the quasi-critical fluids and the kinetics of the extraction process.

Figure 2 shows a layout of the high pressure Soxhlet extractor. This unit is initially charged with a sample of ground solid material to be extracted, and operates at total reflux of the solvent. After a fixed number of cycles is completed, the unit is decompressed and the final product is obtained. Liquid carbon dioxide and propane were used in the experiments, as pure solvents at near-critical conditions. Table 1 shows the composition of the rosa mosqueta oil obtained by high-pressure extractions using the solvents mentioned above. Also included in the table, for comparison, are the results of classical extractions using hexane at atmospheric pressure.

The operating conditions and product yields are given in Table 2.

Figure 3 shows a scheme of the flow type unit. A continuous flow of solvent is compressed and heated up to the operating conditions at the extraction chamber, which was previously filled with ground oil-seeds. Thermodynamic equilibrium is reached by using an adequate flow of solvent. The solvent is then expanded into the separator, through a heated micrometering valve. The oil precipitates into a glass-wool trap, and the oil-free solvent passes into a flow-metering device.

Table 3 shows the solubility of rosa mosqueta oil in carbon dioxide (extract phase) at near-critical conditions. As it can be seen, the solubility of rosa mosqueta oil in carbon dioxide is very low at near-critical conditions. In this region, the solubility decreases with increasing temperature, due to the decrease of the solvent density. In order to increment the solubility, the pressure should be raised above 300 bars. Another alternative is to analyse the effect of co-solvency, which will require a lower level of pressure.

Table 4 shows the increase in solvent power caused by the use of propane as a co-solvent.

5. Discussion

The oil obtained by using any of the three solvents studied (carbon dioxide, propane and hexane) shows a similar composition in triglycerides and tocopherols (see Table 1). However, extractions with carbon dioxide produces a more translucent product, due to the selectivity of this solvent towards products of lower polarity and molecular weight; i.e. no pigments and waxes from the seeds are extracted.

An economically viable process should keep the selectivity of carbon dioxide, but allowing the extraction to be carried out at lower operating pressures to reduce operating and capital costs. The use of propane as a co-solvent arises as a good alternative, because it improves the solvent capacity of carbon dioxide, without affecting its selectivity significantly. This, in turn, reduces the operating pressures. On the other hand, propane is much more volatile than hexane, which facilitates the solvent removal and final conditioning of the oil. Further research in this direction is being carried out.

6. References

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Table 1 - Composition of Rosa Mosqueta Oil (weight %)

Fatty acids	Hexane	Carbon dioxide	Propane
Palmitic acid	3.46	3.65	3.25
Stearic acid	1.52	0.89	1.68
Total Saturated	4.98	4.54	4.93
Oleic acid	15.71	15.40	16.18
Total Mono-unsaturated	15.71	15.40	16.18
Linoleic acid	45.68	45.16	44.16
Linolenic acid	33.63	34.90	34.73
Total Poly-unsaturated	79.31	80.06	78.89
Tocopherol (ppm)	$\alpha = 144$ $\gamma = 613$ $\delta = 50$	$\alpha = 178$ $\gamma = 890$ $\delta = 58$	$\alpha = 194$ $\gamma = 812$ $\delta = 69$
Peroxide value meq/1000g sample	1.19	1.63	-
Phosphorus content (ppm)	11.5	0.0	3.0

Table 2 - Operating conditions and product yields

Solvent	Solvent wt. (gr.)	Seed wt. (gr.)	Temp. (°C)	N° of Cycles	Time (min)	Pressure (bar)	yield (wt %)
Hexane	250.	30.	65.0	5	75.0	1.0	10-11
Propane	250.	30.	10.0	6	90.0	6.3	6-7
Carbon dioxide	250.	30.	15.0	22	330.0	52.0	7-8

Table 3 - Solubility of rosa mosqueta oil in carbon dioxide (extract) at different temperatures (T) and pressures (P)

P (bar)	T (°C)	g oil/100Kg carbon dioxide
70	20	83
70	40	9.80
70	60	3.24
90	60	4.11

Table 4 - Extractions with carbon dioxide propane mixtures at 70 bar and 40°C

% Propane	g oil/100Kg solvent
0.0	9.8
86.0	950
95.0	2400
97.0	2670

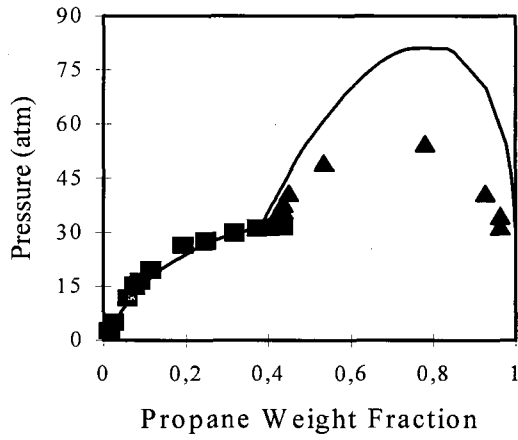


Figure 1 - Propane - sunflower oil mixtures at 353K Exp. VLE (■) and LLE (▲) data from de la Fuente (1994).
 — GC - EOS predictions

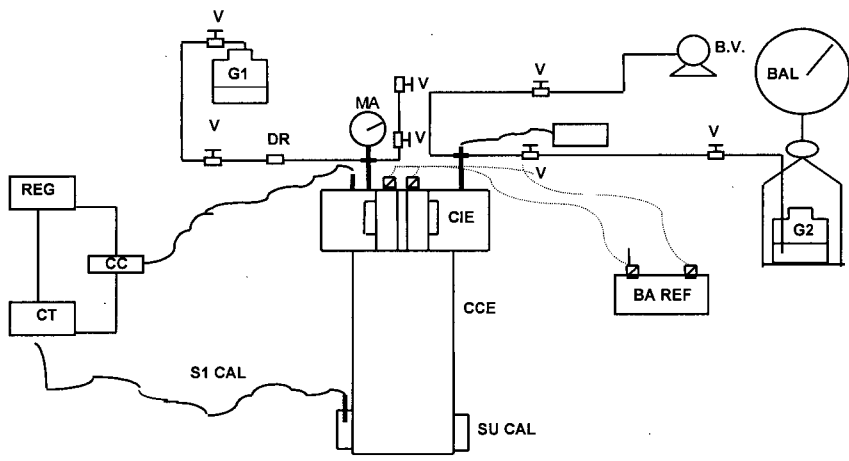


Figure 2 - High pressure Soxhlet extractor. V: valves; G1: inert gas; G2: working fluid; MA: pressure gauge; CIE: clamp closure; CCE: body cell; BA REF: cooler; SU CAL: heating tape; BAL: balance; B.V.: vacuum pump; REG: register; CC: cycle counter; CT: temperature controller; S1CAL: temperature sensor; DR: rupture disk.

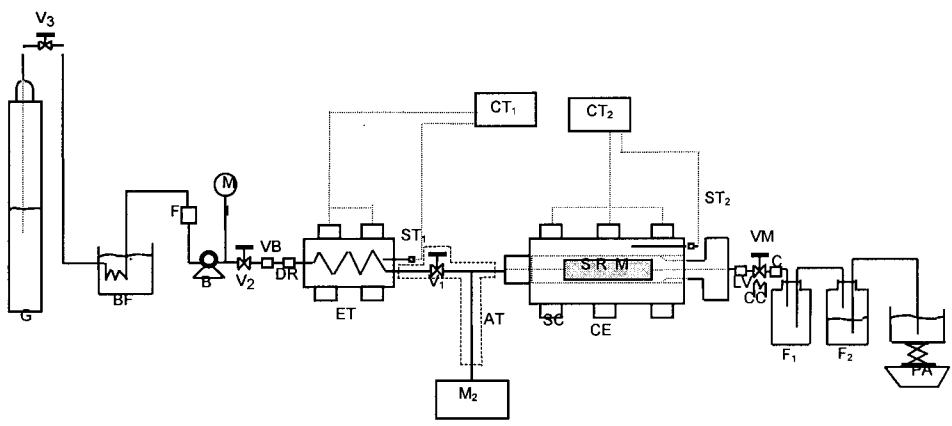


Figure 3 - Flow type unit. G: gas cylinder; V: valves; BF: cold bath; F: filter; B: pump; M: pressure gauges; DR: rupture disk; SC: heaters; ET: thermostated; ST: temperature sensor; CT: temperature controller; AT: thermal isolation; CE: extractor; SRM: seed sample; LV: filter; VM: micrometering valve; CC: heating tape; CP: glass-wool trap; F: flow metering device; PA: balance.