Supercritical Fluid Extraction of Sunflower Seed Oil with CO_2–Ethanol Mixtures

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ABSTRACT: The effect of ethanol addition to supercritical carbon dioxide (SC–CO_2), up to 20%, on sunflower seed oil extraction over the range of 150 to 350 bars and 42 to 80°C was studied. A nonrecirculating home-made bench-scale system was used as extraction equipment. The oil-SC-CO_2–ethanol mixture was reduced to atmospheric pressure in a test tube, where two phases, oil and ethanol, were obtained and ethanol-saturated CO_2 was liberated to the atmosphere. Results show that sunflower oil solubility in SC–CO_2 greatly increases with addition of ethanol as entrainer over the whole range of pressure and temperature conditions. Some phospholipids are co-extracted at levels directly proportional to the added ethanol. Moreover, a large amount of phospholipids was recovered in the ethanolic phase. Acidity of the extracted oil with ethanol as entrainer was lower than that without alcohol. Part of the free fatty acids was found in the ethanolic phase.
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KEY WORDS: Entrainer, oil acidity, phospholipids, supercritical CO_2–ethanol mixtures, supercritical extraction of oil.

Previous studies (1–3) have shown the feasibility of supercritical carbon dioxide (SC–CO_2) extraction of oils from several plant seeds, including sunflower seeds (4), to render products of similar or better quality than oils obtained by organic solvent extraction. To upgrade those bench-scale results to industrial production, processes for oil separation from SC–CO_2 and recirculating SC–CO_2 should be proposed. Calvo and Cocero (5) showed that this can be achieved for sunflower oil by reduction of pressure but not by changes in temperature if operated at moderate pressures.

An economic analysis of the extraction process of soybean oil with SC–CO_2 (6) shows that the operating costs are only comparable to the extraction process with hexane when oil recovery is achieved by temperature variation at 600 bar. But operating at this pressure, capital costs are high (7). To reduce this cost, it would be necessary to operate at moderate pressures and to recover the oil only by changing temperature.

Preliminary results for palm oil from Brunner and Peter (8) showed that addition of an entrainer could make regeneration of the solvent possible by only a temperature change and increased oil solubility. However, these benefits must be balanced against the disadvantage of co-extraction of undesirable compounds, such as phospholipids (PL) and free fatty acids (FFA).

The objective of this work is to study the effect of ethanol addition as modifier on solubility and selectivity in the extraction process of sunflower oil. Operating conditions will be analyzed to achieve oil recovery by changing temperature while working at moderate pressures.

MATERIALS AND METHODS

Materials. Sunflower seeds, dried (overnight at 60°C) and finely chopped with a coffee grinder, were used to obtain oil samples. The size distribution of the seed particles is presented in Table 1. Average particle size was 0.5 mm, and initial oil content was 31% (7). CO_2, industrial grade (99.5%), was drawn as a liquid at 50 bars (Air Liquid, Valladolid, Spain). Absolute ethanol (99.5%; PANREAC, Barcelona, Spain) was used as modifier. Compounds used as reagents in acidity and phosphorus determinations were of analytical grade from PANREAC.

EXPERIMENTAL PROCEDURES

Apparatus. A general scheme of the apparatus is shown in Figure 1. Two membrane pumps (Milroyal D; Dosapro Milton Roy, Madrid, Spain) connected in parallel, which can op-

TABLE 1
Size Distribution of Chopped Sunflower Seed[a]

Sieve size	>1.4	0.9–1.4	0.63–0.9	0.45–0.63	0.30–0.45	0.0010–0.30	<0.010
Mass fraction (%)	6.7	13.1	7.0	19.2	1.2	47.6	5.2

[a]Average particle size is 0.5 mm.

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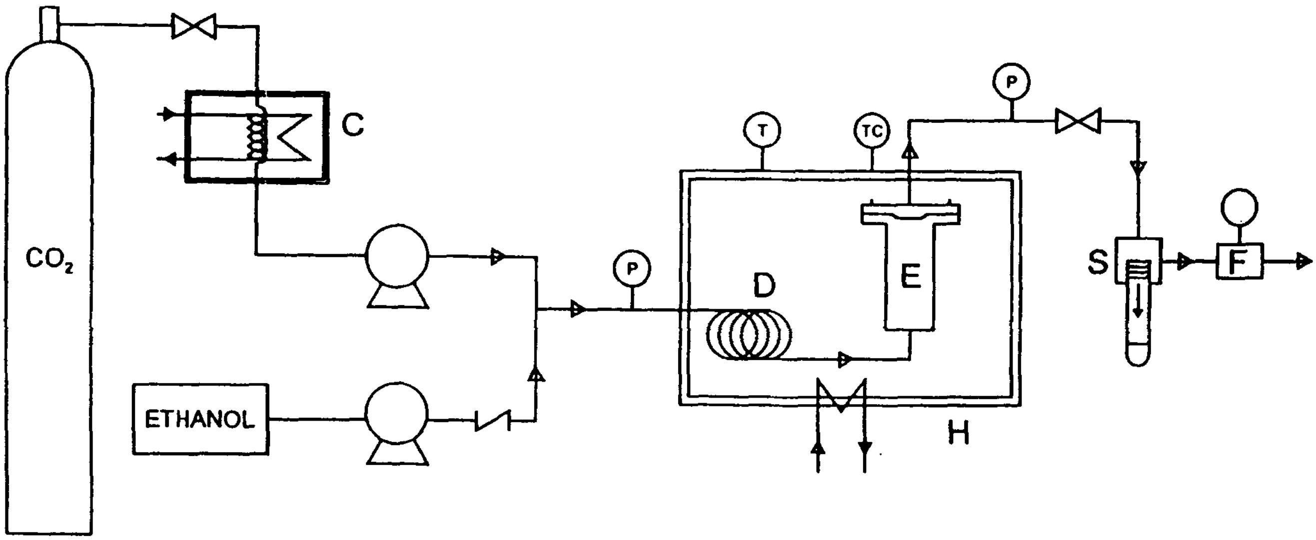

FIG. 1. Schematic diagram of the experimental extraction system: (C) cooler; (D) temperature equilibration coil; (E) extraction vessel; (H) oven; (S) sample collection vessel; (F) volumetric flow meter.

erate in the range of 1 to 10 mL/min, were used to pump CO_2 and the modifier up to the extraction pressure. Both pumps have a back-pressure relief valve, and the one for CO_2 has an attached chamber in which a cooling fluid flows to maintain it operating at −20°C. Ethanol was entered in different proportions to the CO_2 mass, calculated from the total volume indicated by the outlet flow meter at 20°C and atmospheric pressure. Operating temperature was reached by passing the CO_2–ethanol mixture through a coil placed inside a temperature-controlled (±1°C) oven. The 0.1-L extraction vessel, placed in the oven, consisted of a thick-wall cylinder made of 316 stainless steel that was sealed hermetically at the head by a conical closure with a top. Pressure was adjusted by a pressure relief valve, working in a range of 70 to 450 bars with an accuracy of ≤2%. The valve was inserted into an aluminum block, maintained at 65–70°C to avoid freezing. Solute was recovered at the bottom of the receiver, while CO_2 passed through a totalizer flow meter before being exhausted.

Extraction procedure. A ~55-g chopped seed sample was placed into the 0.1-L extractor. A stainless-steel filter mesh screen was placed at each end of the extractor to prevent any carry over of particles. The extractor was then introduced into the temperature-controlled chamber. Care was taken to ensure that air was purged before extraction was started (4). The appropriate CO_2 and ethanol amount was pumped up to extraction pressure and directed into the bottom of the extractor. The supercritical phase solution left the extractor and reached the valve where pressure was reduced to atmospheric conditions. The oil–ethanol mixture was collected in a test tube while ethanol-saturated CO_2 left through the gas meter. Successive oil samples of roughly 1 g were collected with their correspondent ethanolic phase from each seed load until oil exhaustion (after 30 min of passing the solvent mixture, no oil was collected). Afterwards, the mixture was separated into two phases by centrifugation at 3000 × g for 5 min. The amounts of ethanol recovered for 20, 15, 10, and 5% of ethanol entered in the feed were 10.1, 7.1, 5.1, and 3.0%, respectively. Residual ethanol in oil was <0.3% while <0.02% of oil remained in the ethanolic phase. The experimental error in the determination of oil solubility was greater than the effect caused by the presence of ethanol remaining in the oil. Therefore, this effect was considered negligible.

Oil solubility and PL and FFA concentrations were measured within the range of 150 to 350 bars for pressure, 42 to 80°C for temperature and increasing amounts of ethanol (5, 10, 15, and 20% w/w).

Oil solubility measurements. Solubility data, represented in the figures, correspond to the slopes of the linear part of the extraction curve for each condition (5). Results are given as mg oil/g CO_2 that passed through the seed bed to obtain the collected oil. Each solubility data point was obtained by linear regression of at least 12 points, from the linear part of the extraction curve and repeated at least twice.

Acidity determination. Oil acidity was determined by Standard Method II.D.1 of the American Oil Chemists' Society. Before, oil was bubbled with N_2 for 2 h to remove dissolved CO_2 which could contribute to acidity (9). Acidity in the ethanolic phase was directly titrated with KOH dissolved in ethanol.

Determination of PL content. PL concentration in the oil was indirectly determined as ppm of phosphate–phosphorus. The method was based on the one described by Duck-Chong (10) for determining PL by digestion with magnesium nitrate. Total oil phosphorus was converted to inorganic phosphate by digesting a sample of 0.3–0.5 g of the oil with 2 mL of magnesium nitrate solution, 10% (wt/vol) $Mg(NO_3)_2 \cdot 6H_2O$ in methanol. Digestion was achieved by ashing the sample in a microwave furnace (Milestone MLS 1200, Pyro Milestone

S.R.L., Sorisole, Italy), where the temperature was gradually increased to 600°C and held constant for 20 min. White powder so obtained was dissolved in 5 mL of 1 M HCl. Inorganic phosphate was then determined by a colorimetric method (11). Standards that contained 0.5–100 µg of inorganic phosphate–phosphorus (KH_2PO_4) were added to oil samples free from phosphorus and digested as described above to develop a standard curve of concentration vs. absorbance. The low detection limit of the method was estimated to be 2 ppm. The same procedure was used to determine PL dissolved in the ethanolic phase. Phosphorus concentrations in the ethanolic phase are based on the amount of ethanol collected.

RESULTS AND DISCUSSION

In a previous report, sunflower oil solubility was shown to increase with pressure and to decrease with temperature up to the crossover point (400 bar). Moderate pressure, 300 bars, was used to compare the effect of ethanol addition. Oil solubility appears to be directly proportional to ethanol content (Fig. 2). The rate of increase was about 5 mg/g CO_2 for each 1% (weight basis) increase in ethanol content.

PL are not soluble in SC–CO_2 (3). However, addition of low concentrations of ethanol causes the extraction of small concentrations of phosphorus (12,13). In Figure 3, the total amount of phosphorus present in the oil and ethanolic phase is presented as a function of ethanol concentration in the feed. An increase in ethanol concentration causes an increase in phosphorus solubility. Similar results have been found for egg yolk (14). On the other hand, the phosphorus content was distributed between oil and its corresponding ethanolic phase, which contained the larger amounts of phosphorus (Fig. 4). Taking into account that PL presence is undesirable for oil quality and the important increase of phosphorus with ethanol content, it would be advisable not to add more than 10%.

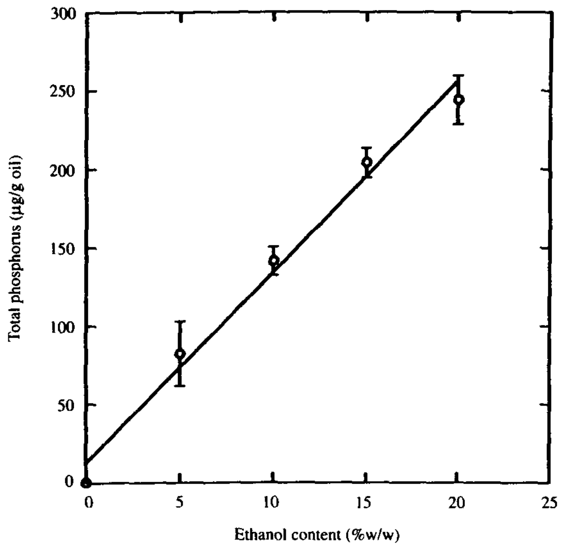

FIG. 3. Total extracted phosphorus, expressed as µg phosphorus/g of extracted oil, as a function of the amount of ethanol added to CO_2 at 42°C, 300 bars: ○, experimental data; solid line, linear fitting.

Oil solubility also depends on both pressure and temperature conditions at a fixed ethanol concentration, as shown in Figures 5 and 6. High-pressure values lead to increased oil solubility, regardless of the amount of ethanol added. Nevertheless, the effect of pressure is greater when a greater quantity of ethanol is used. For example, at a temperature of 60°C and 5% ethanol, an increase in pressure from 200 to 350 bars results in an increase of ~20 mg oil/g CO_2 in oil solubility, while the increase in solubility is more than 40 mg/g CO_2 at

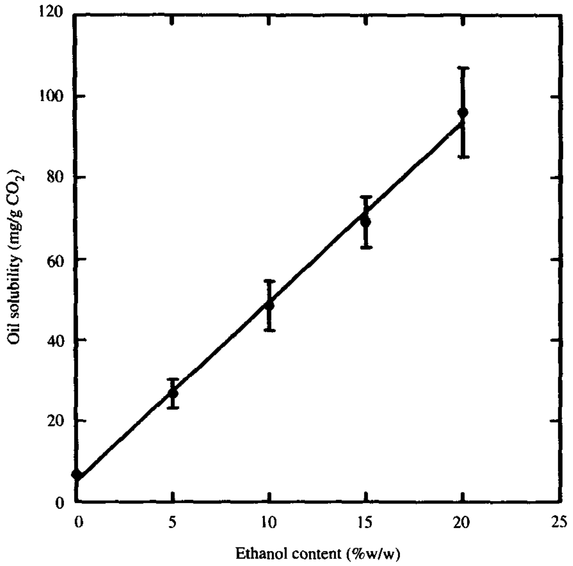

FIG. 2. Solubility of sunflower oil in CO_2, modified with ethanol, at 42°C and 300 bars. The error bars represent the range of slopes of the linear portion of each extraction curve: ●, experimental data; solid line, linear fitting.

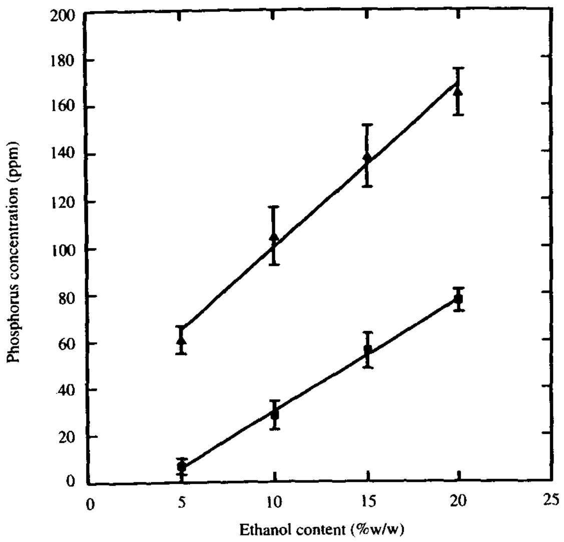

FIG. 4. Phospholipid content, expressed as ppm of phosphorus in collected oil and ethanolic phases, as a function of the amount of ethanol added to CO_2 at 42°C, 300 bars: ▲, ethanolic phase; ■, oil; solid lines, linear fitting.

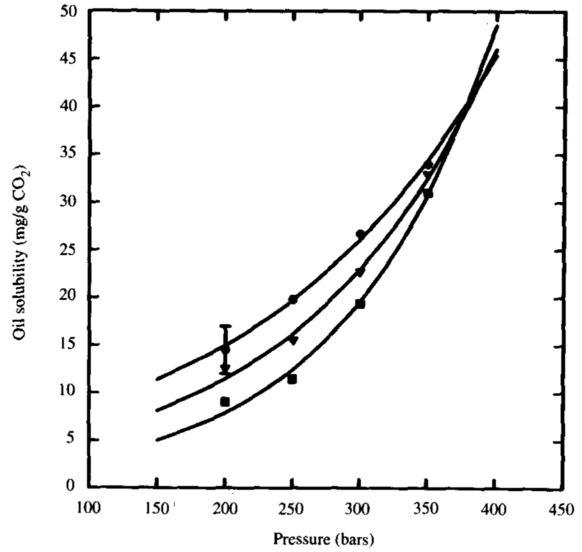

FIG. 5. Solubility of sunflower oil in CO_2, modified with 5% ethanol, as a function of pressure at different temperatures: ●, 42°C; ▼, 60°C; ■, 80°C; solid line, exponential fitting.

10% ethanol addition. The effect of temperature on oil solubility also varies with ethanol level. The change in oil solubility with temperature is greater at the 10% ethanol level. For example, at 250 bars, a decrease in temperature from 80 to 42°C with 10% ethanol causes an oil solubility increase of 15 mg oil/g CO_2, while at 5% ethanol it is about 8 mg oil/g CO_2. With CO_2 alone, an increase of only 3 mg oil/g CO_2 is found between these temperatures. Moreover, ethanol addition causes convergence of the solubility isotherm at a lower pressure, resulting in the displacement of the crossover point from 400 bars for neat CO_2 to 375 bars and 350 bars for 5 and 10% ethanol addition as modifier, respectively.

Pressure and temperature also influence the phosphorus concentration of the extract. While the effect of pressure and temperature on phosphorus content was minimal at low ethanol concentration, (at 5% ethanol, the quantities found in oil were always less than 10 ppm), it was appreciable at 10% ethanol. Figure 7 shows that phosphorus content increased with pressure and decreased with temperature within the range of conditions tested. The distribution of phosphorus content between oil and ethanol at 20°C and atmospheric pressure of the separation conditions is presented in Figure 8. In optimization of the process, it will be taken into account that quantities of PL extracted are minimized by working at low pressures and at least 60°C.

The phosphorus concentration of all fractions of each load was determined and a decrease in phosphorus concentration of the final fractions of both phases was observed during oil exhaustion (Fig. 9). It seems that PL are extracted with triglycerides (TG) simultaneously. Even when oil is totally exhausted, no increase in PL content is detected in the ethanolic phase, although the residual PL content in the seed is still high. Fractionation was detected in FFA content of the extracts. Acidity of oil samples decreased as extraction progressed with SC–CO_2 alone or with ethanol (Fig. 10). Moreover, Figure 10 indicates that addition of ethanol would reduce acidity, for all oil fractions combined, from 1.9% for CO_2 alone to 0.4% with 10% ethanol. Part of the extracted FFA was retained in the ethanolic phase, in which they are quite soluble. Average acidity in the ethanolic phase was ~0.7% as oleic acid. The first fractions could be eliminated to reduce the acidity of the product.

Practical implications. Higher extraction yield was achieved with increasing ethanol concentration in the CO_2 feed. However, it is necessary to optimize the ethanol concentration as well as pressure and temperature of the extrac-

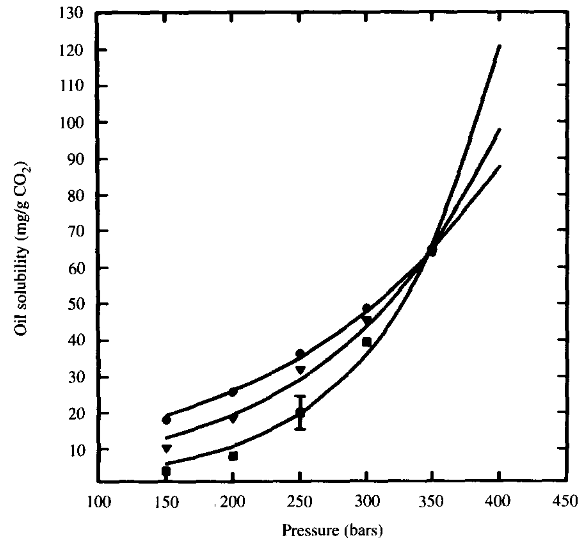

FIG. 6. Solubility of sunflower oil in CO_2, modified with 10% ethanol, as a function of pressure at different temperatures: ●, 42°C; ▼, 60°C; ■, 80°C; solid line, exponential fitting.

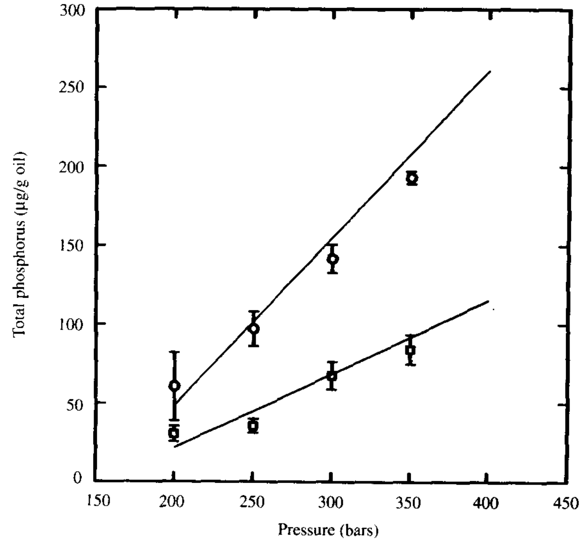

FIG. 7. Total extracted phosphorus per g of oil as a function of pressure at different temperatures for CO_2 modified with 10% ethanol: ○, 42°C; □, 60°C; solid line, linear fitting.

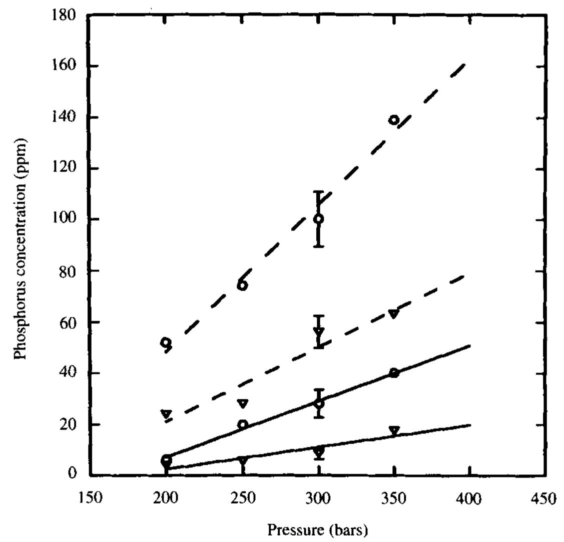

FIG. 8. Phospholipid content expressed as ppm of phosphorus, in collected oil and ethanolic phase, for CO_2 modified with 10% ethanol, as a function of pressure at different temperatures: ○, 42°C; ▽, 60°C; solid line, linear fitting of phosphorus concentration in oil; dashed line, linear fitting of phosphorus concentration in ethanolic phase.

tion conditions to get the maximum yield of TG while minimizing phosphorus in the extract. Although greater solubility is obtained at higher working pressures, solubility enhancement from ethanol as an entrainer would permit operation at lower pressures. At 200 bars, 60°C and 10% ethanol, oil solubility is ~20 mg oil/g CO_2, while a negligible amount was found in CO_2 alone under the same conditions.

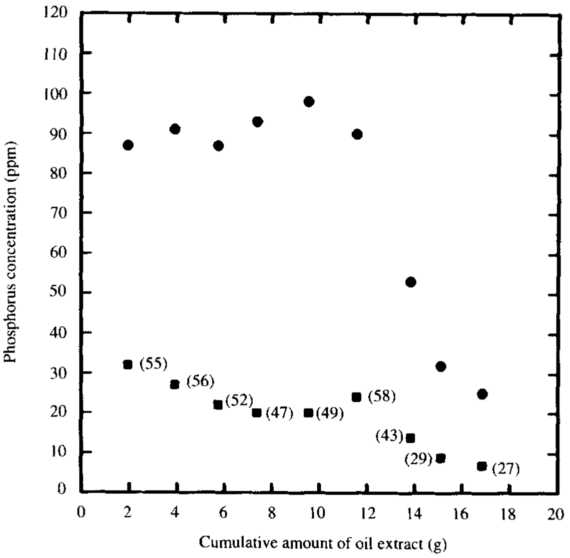

FIG. 9. Phosphorus concentration plotted vs. oil mass, extracted in successive samples of the same load. Numbers in parentheses are oil solubilities in the samples expressed as mg oil/g CO_2. Extraction conditions: initial seed mass ~55 g, 10% ethanol, 300 bars, 42°C, CO_2 flow rate: 0.85 g/min: ■, oil phase; ●, ethanolic phase.

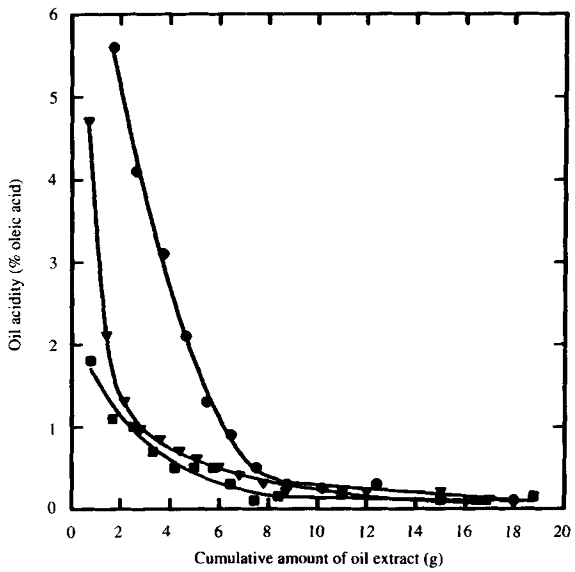

FIG. 10. Acidity of oil samples, extracted consecutively from the same load. Extraction conditions: initial seed mass ~55 g, 300 bars, 42°C, CO_2 flow rate: 0.85 g/min (●, CO_2 alone; ▼, CO_2 modified with 5% of ethanol, ■, CO_2 modified with 10% ethanol).

Addition of ethanol improves the pressure effect on oil solubility. Consequently, in a continuous process, oil separation by a decrease in pressure would be more effective as more ethanol is added. This fact is important because solvent recycling could be possible by low recompression relations.

By using ethanol as an entrainer, oil separation can be achieved by a temperature change at moderate pressures. Depending on the working pressure, either heating or cooling is necessary to reduce oil solubility. For example, at 400 bars and 80°C, oil solubility is reduced when temperature is decreased to 42°C. On the contrary, if operating at 200 bars, the oil solubility reduction would be obtained by an increase in temperature from 42 to 80°C.

Further work is needed to decide which of these possibilities is the most suitable. It will be necessary to operate while recirculating the solvent mixture and to study the economic and technical feasibility of each proposed process.

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