

Use of Liquid Carbon Dioxide to Remove Hexane from Soybean Oil

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ABSTRACT: Liquid carbon dioxide (L-CO₂) was investigated as a means to separate hexane from the mixture of soybean oil (SBO) and hexane resulting from the hexane extraction of soybeans. Using a fractionation tower, 5 vol of CO₂ (i.e., 100, 200, 300, 500, and 1000 L expanded gas) were passed through 50 mL of two concentrations of *n*-hexane (i.e., 10 and 25% w/w) in SBO. After passing through the hexane/SBO mixture, the expanded CO₂ was passed through a chilled collection flask to capture extracted hexane and SBO. The raffinate SBO was removed from the column and analyzed for residual hexane using International Organization for Standardization Method 9832:2002. Residual hexane decreased as the amount of L-CO₂ used increased and was less than 20 ppm after 200 L of CO₂. The amount of SBO extracted increased with the volume of CO₂ used. Significantly more SBO and hexane were collected from the 25% sample than the 10% sample. During the extraction of the mixture, the CO₂ selectively carried over TG with lower M.W. This research demonstrates the ability to use L-CO₂ to remove hexane from mixtures of hexane and SBO at both low pressures and temperatures.

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Although supercritical carbon dioxide (SC-CO₂) has been studied as a replacement for hexane extraction of oilseeds (1,2) and SC-CO₂ extractions have many advantages over hexane extraction (3), SC-CO₂ is not currently economically viable for large-scale oilseed processing. This is due to the low bulk value of seed oils, high capital costs of SC-CO₂ extraction, and the inconvenience of batch processing large quantities of solid materials such as soybeans under high pressure (4).

Soybean oil (SBO) is currently extracted on an industrial scale using hexane, and the largest operating cost is the separation of hexane from the extracted oil, which involves heated evaporators and reduced-pressure strippers (5). Currently, the hexane/SBO mixture (i.e., miscella) is desolventized by double-effect evaporation and steam stripping (6). Typically, the miscella leaving the extractor contains *ca.* 75% hexane and

25% oil (7). The total energy required to vaporize the hexane is a function of the heat of vaporization of hexane, which is 80.2 cal/g (8), and the amount of hexane present. Approximately 660 kJ/kg SBO (as steam) is used in the evaporator and stripper to separate the hexane from the SBO (5).

Recently, it was demonstrated that SC-CO₂ at 12 MPa and 40°C could be used to remove hexane from a 10% w/w mixture of hexane and SBO using a countercurrent packed tower giving residual hexane levels as low as 20 ppm (9). A 10% w/w mixture of hexane and SBO is representative of the hexane concentration after the second evaporation stage. Reverchon *et al.* (9) examined three temperatures (i.e., 40, 50, and 60°C) in combination with 12 MPa and found that residual hexane decreased with extraction temperature and that residual hexane was inversely proportional to CO₂ density. Because the density of CO₂ at 12 MPa is significantly higher at 25°C (i.e., 0.87 g/mL) than at 40°C (i.e., 0.73 g/mL) (SF Solver Program; Isco Inc., Lincoln, NE), it seemed likely that at temperatures cooler than 40°C (e.g., 25°C), residual hexane could be even less using liquid CO₂ (L-CO₂). Hexane is miscible with L-CO₂ at 25°C (10), whereas the solubility of SBO in L-CO₂ at 25°C is *ca.* 0.1% by weight (11). Because the costs of CO₂ extractions are proportional to both the pressure used and the extraction temperature, L-CO₂ extractions are significantly less costly than SC-CO₂ extractions, which are done at both higher pressures and higher temperatures than L-CO₂ extractions.

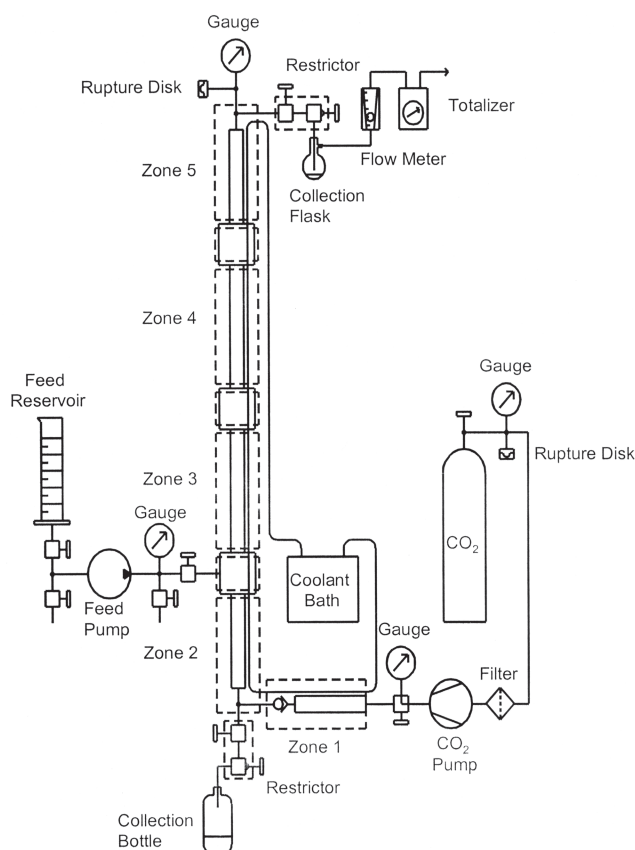
The purpose of this study was to investigate the use of L-CO₂ (i.e., lower pressure and temperature) in place of SC-CO₂ to remove hexane from a hexane/SBO mixture and to determine the amount of L-CO₂ required to effectively separate the hexane. We examined two concentrations of hexane in SBO (i.e., 25 and 10% w/w) representing the concentration of hexane after the first and second stage evaporators. In addition, we examined the amount of SBO that was carried over with the L-CO₂ and the collection of separated hexane, and compared the FA compositions of the extracted SBO and the SBO left behind (i.e., the raffinate). An energy comparison with the conventional process was not an objective of this study.

EXPERIMENTAL PROCEDURES

Fractionation column. The L-CO₂ extractions were performed in a stainless-steel fractionation column previously

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SCHEME 1

described (12), with the modifications shown in Scheme 1. The column has a total height of 253.2 cm and an internal volume of 412 mL. The column includes a precooling section and four separate zones, each having an internal diameter of 1.43 cm and a height of 63.3 cm. The column was packed with protruded stainless-steel packing (0.41 cm Pro-Pak; Cannon Instrument Company, State College, PA) that provided 94% void volume. Extraction zones were maintained at 25°C by being wrapped with silicone tubing attached to a refrigerated circulating bath. Glas Col heating mantles enclosed each zone and were independently controlled to heat the column to the desired temperature for postextraction cleanup. The temperature was monitored by Type-J thermocouples attached to the column wall. Thermocouples were also inserted into the column at junctions to monitor internal column temperature.

SBO/hexane mixtures. The hexane/SBO mixtures were prepared by mixing HPLC-grade hexane (Fisher Scientific, Fair Lawn, NJ) and refined-bleached-deodorized (RBD) SBO purchased locally (Aldi Carlini soybean oil) to give solutions containing 10 and 25% w/w *n*-hexane. These mixtures were placed in glass bottles filled to the rim (i.e., no headspace) to prevent loss through vaporization of hexane, sealed, and held at -70°C until used in experiments. The densities of these mixtures were determined using a U.S. Standard Mini Weight Per Gallon Cup (Paul N. Gardner Company, Inc., Pompano Beach, FL) and found to be 0.886 and 0.844 g/mL for the 10 and 25% solutions, respectively.

Desolventizing experiments. Welding-grade CO₂ was fed from a cylinder and passed through a filter containing alumina C to a gas booster pump. The column was pressurized to 9.3 MPa, and the CO₂ (0.823 g/mL) entered the column, passing through the hexane/SBO mixture as it moved upward. The hexane/SBO mixtures (50 mL) were introduced into the column by a liquid metering pump connected to a stroke counter controller. Mixtures were fed into the column between zones 2 and 3. The solute-laden CO₂ flowed up the column and exited as expanded gas at a flow rate of ca. 4 L/min (STP) across a micrometering valve, allowing the extract to be collected in a tared 100-mL round-bottomed flask chilled with dry ice/acetone. The gas stream passed through a dry test meter (model DTM-200A; American Meter Corp., Horshana, PA) to measure the total gas volume and was then vented to the atmosphere. The total mass of recovered hexane and SBO was measured, and the hexane was subsequently removed under a gentle stream of nitrogen at 70°C. The masses of the recovered hexane as well as SBO extracted by the L-CO₂ were determined.

The SBO left in the column (i.e., raffinate) was then collected at the bottom of zone 2 through the valve system and immediately placed in vials filled to the rim to prevent loss through vaporization of any hexane present. The raffinate was analyzed for residual hexane using ISO Method 9832:2002 (13). This method involves GC analysis of the headspace over the SBO with an added internal standard and comparison to a standard curve. Briefly, sealed vials containing the SBO samples (with added cyclohexane internal standard) were heated to 80°C with mixing, and a 1-mL headspace sample was taken using a gas-tight syringe. This sample was subsequently injected into a gas chromatograph to determine hexane concentration.

After each extraction, the fractionation column was cleaned to prevent contaminants from being carried over to subsequent runs. The refrigerated circulating bath was turned off and the column was heated to 80°C and pressurized to 58.6 MPa; then SC-CO₂ (800 L @ STP) was passed through the column at 5 L/min for cleanup.

FA compositional analysis. The FA profiles were determined for both the SBO carried over with the CO₂ and hexane (i.e., extract), the SBO left in the column (i.e., raffinate), and the starting SBO before being subjected to CO₂ extraction. SBO samples (100 mg) were transesterified and analyzed by GC as described previously (14). A single GC analysis was performed on each sample. Because of the limited amounts of oil available, samples were not analyzed for the 100- and 200-L CO₂ treatments.

Statistical analyses. ANOVA were conducted on data using Statistix[®] 7 software (Analytical Software, Tallahassee, FL) and comparisons made using the least significance difference test at the *P* = 0.05 level.

RESULTS AND DISCUSSION

The mean residual concentrations of *n*-hexane for the 10 and 25% hexane/SBO mixtures and the 5 vol of CO₂ used are

TABLE 1
Mean^a Residual *n*-Hexane (ppm) in Soybean Oil Extracted with Liquid Carbon Dioxide

Volume CO ₂ (liters STP) ^b	Residual <i>n</i> -hexane concentration in soybean oil (ppm)	
	10% Hexane solution	25% Hexane solution
100	247.0	128.5
200	11.1	19.8
300	8.0	38.3
500	3.0	13.0
1000	7.1	1.9

^a*n* = 2.

^bCO₂ was passed through 50 mL of the hexane/soybean oil solutions.

shown in Table 1. Overall, the residual hexane concentrations were very low for all treatments considering the original concentrations of hexane were 100,000 and 250,000 ppm for the 10 and 25% solutions, respectively. Even the sample with the highest residual hexane content (i.e., 247.0 ppm) contained only 0.25% of the hexane originally present (i.e., a 99.75% reduction). The ANOVA indicated that there was a significant main effect of liters of CO₂ ($F_{4,10} = 14.64$, $P = 0.0003$) on residual hexane concentration, but that the main effect of hexane concentration ($F_{1,10} = 0.66$, $P = 0.44$) and the hexane concentration \times liters of CO₂ interaction ($F_{4,10} = 2.08$, $P = 0.16$) were not significant. Residual hexane was highest for the lowest amount of CO₂ used (i.e., 100 L), and the residual hexane concentration decreased as the volume of CO₂ increased; however, with volumes over 200 L of CO₂, the decrease was slight. Regression analysis indicated that the residual hexane data followed a first-order decay for both the 10 and 25% mixtures ($R^2 = 0.92$ and 0.98 , respectively). By using conventional methods, residual hexane in SBO after the stripper is typically 1000 ppm (i.e., 0.1%), and the minimum that can be achieved is *ca.* 500 ppm (6), whereas the previous work using SC-CO₂ gave residual hexane of *ca.* 20 ppm from a 10% hexane/SBO mixture (9). Our results indicate that 200 L of L-CO₂ can give residual hexane concentrations below 20 ppm from both a 25% hexane/SBO mixture and a 10% hexane/SBO mixture. This volume of L-CO₂ represents a CO₂/miscella ratio of 8.32 or 8.67 (w/w) for the 10 and 25% solutions, respectively. Because of the inherent efficiency of continuous countercurrent extractions (15), its application to this L-CO₂ method may allow significantly less than 200 L of L-CO₂ to effect the hexane removal. In addition, because high temperatures used during standard desolventizing may adversely affect oil quality due to the formation of nonhydratable phosphatides (16), the low temperatures (i.e., 25°C) used in this L-CO₂ desolventizing method may provide a means to improve oil quality as well.

The effect of liters of CO₂ on the amount of SBO collected is shown in Figure 1. The ANOVA indicated that there were significant main effects of both hexane concentration ($F_{1,10} = 9.82$, $P = 0.01$) and liters CO₂ ($F_{4,10} = 53.51$, $P < 0.0001$) on the amount of SBO collected, but that the hexane concentration \times liters of CO₂ interaction was not significant ($F_{4,10} = 0.62$,

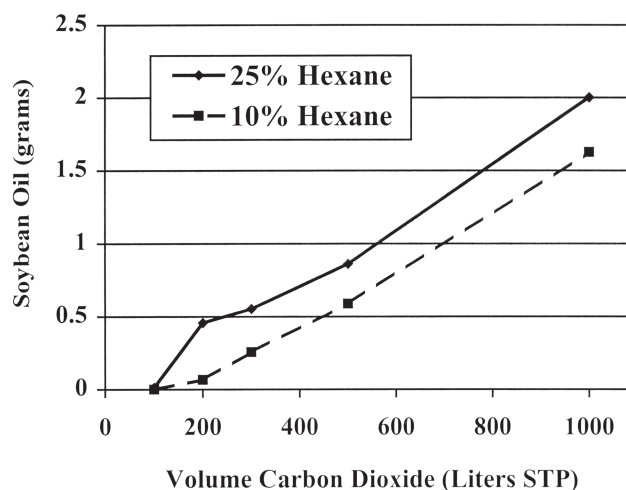


FIG. 1. Grams soybean oil recovered from exiting carbon dioxide as a function of hexane concentration and volume of carbon dioxide (50 mL miscella).

$P = 0.66$). The amount of SBO collected is clearly proportional to the liters of CO₂ used. This is a result of a low solubility of SBO in L-CO₂ and of the total amount extracted being a function of the volume of CO₂ used. In addition, the amount of SBO collected was significantly higher for the 25% hexane sample (overall average of 778.4 mg) than for the 10% hexane sample (overall average of 508.6 mg). This is probably a result of a cosolvent effect of the hexane in the L-CO₂ causing a slight increase in the solubility of SBO in the L-CO₂/hexane mixture over the L-CO₂ alone. Although residual hexane decreases as the amount of CO₂ increases, there is a trade-off between lower residual hexane and higher carry-over of TG. The SBO carried over with the L-CO₂ also was slightly lighter in color than both the original oil and the raffinate, indicating that the compounds responsible for the color of the SBO are not very soluble in L-CO₂ and are subsequently concentrated in the raffinate.

Overall recovery (i.e., mass balance) of SBO was determined by summing the SBO mass collected with the L-CO₂, the mass of the raffinate, and the mass collected with the SC-CO₂ and dividing by the theoretical amount placed in the column (i.e., 39.9 and 31.7 g for the 10 and 25% solutions, respectively). The ANOVA indicated there were no significant effects of hexane concentration ($F_{1,10} = 0.05$, $P = 0.83$), liters of CO₂ ($F_{4,10} = 0.26$, $P = 0.89$), or hexane concentration \times liters of CO₂ interaction ($F_{4,10} = 1.41$, $P = 0.31$). The grand mean recovery was 95.8%. The apparent loss of SBO is most likely due to less than 50 mL actually being introduced into the fractionation column.

The amount of hexane recovered from the hexane/SBO mixtures varied from a low of *ca.* 160 mg to a high of *ca.* 850 mg although there were no obvious trends with treatment. The ANOVA indicated there was a significant main effect of hexane concentration ($F_{1,10} = 23.94$, $P < 0.001$) on the amount of hexane recovered, whereas the main effect of liters of CO₂ ($F_{4,10} = 1.07$, $P = 0.42$) and the hexane concentration

TABLE 2
Mean^a FA Composition After Removal of Hexane from Soybean Oil Using Liquid Carbon Dioxide

FA	Fraction		Unfractionated soybean oil
	Extract	Raffinate	
Lauric	0.37b	0.00a	0.00a
Myristic	0.23b	0.00a	0.00a
Palmitic	12.06b	10.78a	10.85a
Stearic	3.61a	4.38c	4.28b
Oleic	22.60a	24.26b	24.22b
Linoleic	52.50b	51.88a	51.96a
Linolenic	7.90b	7.77a	7.79a
Behenic	0.22a	0.42b	0.41b

^a*n* = 2. Within rows, means without letters in common differ significantly (least significant difference, *P* = 0.05).

× liters of CO₂ interaction ($F_{4,10} = 2.78$, *P* = 0.09) were not significant. Significantly more hexane was recovered from the 25% *n*-hexane mixture than from the 10% hexane mixture (i.e., overall averages of 648.6 and 267.4 mg, respectively). The amount recovered was always well below the amount of hexane initially present in the sample (i.e., 10.55 and 4.43 g, respectively). The residual hexane analysis of the raffinate indicated that virtually all of the hexane was separated from the SBO, but at most, less than 1 g of hexane was recovered. This suggests our collection method using a round-bottomed flask chilled by dry ice/acetone was not effective in capturing the hexane during decompression of the CO₂. A reduced-pressure receiver vessel after the fractionation column may improve hexane capture, and the use of cold mineral oil absorption could decrease hexane losses in vented gases.

FA compositional analysis. The FA profiles for the SBO extracted with the CO₂, the raffinate, and the FA profile of the SBO before fractionation are shown in Table 2. The statistical analyses indicated that for all FA listed, the concentrations in the extract were significantly different from those found in the both the raffinate and starting SBO, whereas the composition of the raffinate was statistically equivalent to the starting SBO, with the exception of stearic acid, which was slightly higher in the raffinate. Hexane concentration did not have a significant effect on FA concentration, with the exception of oleic acid ($F_{1,12} = 6.42$, *P* = 0.026). However, the effect was inconsequential, as the concentration of oleic was 23.27 and 23.59% when the hexane concentration was 10 and 25%, respectively. The statistical analyses also indicated that there was no effect of CO₂ volume (i.e., 300, 500, or 1000 L) on FA percentage for any FA. There were no significant interactions between the main effects of fraction, hexane concentration, and CO₂ volume on the concentration of any FA. It appears that the CO₂ selectively carries over TG with lower M.W. (i.e., lauric, myristic, and palmitic) compared with those with high M.W., such as behenic. In addition, for the FA containing 18 carbons (i.e., stearic, oleic, linoleic, and linolenic), the ratio of the amount in the extract vs. the amount in the raffinate increased with the number of double bonds. This was probably due to a higher solubility in CO₂

for compounds with lower b.p. and higher vapor pressures (e.g., TG with higher degrees of unsaturation).

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