

Enhanced Selective Extraction of Hexane from Hexane/Soybean Oil Mixture Using Binary Gas Mixtures of Carbon Dioxide

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Carbon dioxide (CO₂) can effectively separate hexane from a mixture of soybean oil (SBO) and hexane with a slight coextraction of SBO. Previous research demonstrated that CO₂ entrained with helium significantly reduced SBO solubility in CO₂. In this study, CO₂ was mixed with three gases (He, N₂, or Ar) (0.5–30 vol %) to decrease SBO solubility while attempting to maintain hexane solubility. The binary gas mixtures (at 25 °C and 9.31 MPa) were passed through a 25 wt % hexane/SBO mixture inside a 2.5 m fractionation column. Coextracted SBO was inversely proportional to binary gas concentration, whereas residual hexane in the raffinate was proportional to binary gas concentration. The 10% binary mixture of N₂ or Ar was the best compromise to obtain both low residual hexane levels (i.e., 26 ppm) and low SBO coextraction (i.e., only 40 mg). This carry-over of SBO represents a 95% reduction in SBO carry-over compared to neat CO₂.

KEYWORDS: Carbon dioxide; binary mixture; selective extraction; soybean oil; hexane

INTRODUCTION

Soybean oil (SBO) is produced industrially by hexane extraction, and the largest operative cost is the distillation of the hexane from the SBO, which involves heated evaporators and heated reduced-pressure strippers (1). The removal of hexane from the SBO is critical because of hexane's demonstrated toxic effects, including nerve damage (2). Hexane elimination from SBO has been investigated using supercritical carbon dioxide (SC-CO₂) (3) and liquid carbon dioxide (L-CO₂) (4, 5), both of which have been demonstrated to effectively separate the hexane from a mixture of SBO and hexane (i.e., miscella). The use of CO₂ to eliminate hexane from SBO is a potential substitute for the energy-intensive methods currently used and may lower costs (3). This separation is possible because the solubility of hexane is very high (i.e., miscible) (6), whereas SBO is only very slightly soluble (e.g., ca. 0.1 wt %) in CO₂ at 25 °C and 10 MPa (7). Although residual hexane levels in the SBO have been reduced to very low concentrations (e.g., <10 ppm) using CO₂ (3–5), one disadvantage is that there is a slight carry-over (ca. 2 wt %) of SBO that is coextracted with the hexane as the CO₂ passes through the miscella (4, 5).

A potential solution to this problem is the use of binary mixtures of other gases in combination with the CO₂ instead of using neat CO₂. Previous research has shown that as little as 5 vol % of nitrogen (N₂) or argon (Ar) mixed with CO₂ can reduce

the solubility of caffeine in CO₂ up to 50% (8). Retention times in supercritical fluid chromatography (SFC) have also been shown to be longer when using CO₂ that has been pressurized with helium (He) (9–12) due to a decrease in the solvating power of the CO₂ with dissolved He compared to neat CO₂. In addition, the solubility of cholesterol in helium head pressure CO₂ (HHP-CO₂) was ca. one-third that of pure CO₂ (13), and the solubility of SBO triglycerides was reduced 50–70% for HHP-CO₂ compared to pure CO₂ (14). The solubility of SBO triglycerides has been shown to be inversely proportional to the concentration of He in CO₂ (15).

It has often been observed that lowering the solvent power is combined with an enhancement of its selectivity (8). Using a binary mixture of nitrogen in CO₂, it was reported that a trace pesticide could be extracted very effectively while the interfering triglycerides could be left behind (16). Although this previous work used SC-CO₂, it was hypothesized that the underlying principle would apply to L-CO₂ as well and that binary mixtures of L-CO₂ could be used in an analogous manner to allow the removal of hexane from miscella while leaving the triglycerides behind. Because the costs of CO₂ extractions are proportional to both the extraction pressure and temperature, L-CO₂ extractions are less costly to perform than SC-CO₂ extractions. The objective of this study was to determine if binary mixtures of gases such as He, N₂, or Ar could be used with L-CO₂ (25 °C and 9.31 MPa) to enhance the selective extraction of the solvent hexane from miscella while coextracting as little SBO triglycerides as possible.

EXPERIMENTAL PROCEDURES

Fractionation Column. The L-CO₂ extractions were performed in a stainless steel column described previously (4, 17). A schematic of

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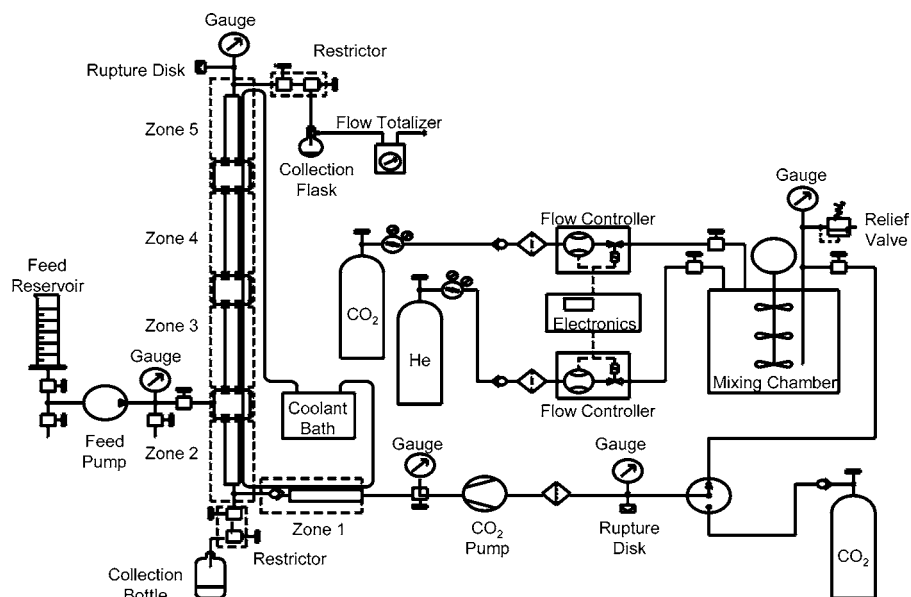


Figure 1. Schematic of fractionation column and binary gas mixing apparatus.

the column with the gas flow controllers and mixing chamber used to produce the binary gas mixtures is shown in **Figure 1**. The column has an internal diameter of 1.43 cm, a height of 253.2 cm, and an internal volume of 412 mL and was packed with protruded stainless steel packing (0.41 cm Pro-Pak) (Cannon Instrument Co., State College, PA) with a 94% void volume. The column was held at 25 °C by being wrapped with silicone tubing that was attached to a Neslab model RTE-220 refrigerated circulating bath (Neslab Instruments, Inc., Newington, NH). Glas Col heating mantles enclosed the column and were used to heat the column during the postextraction cleanup.

Solutions of 25 wt % *n*-hexane in SBO were prepared as described previously (4), and 50 mL (ca. 42.2 g) of the solution were introduced into the column above zone 2 using a Haskel model MS-188 liquid metering pump (Haskel International Inc., Burbank, CA).

Welding-grade CO₂ (Airgas Inc., Radnor, PA) was fed from a cylinder and passed through a filter containing alumina C to a Haskel model AG-30 gas booster pump (Haskel International Inc.).

The column was pressurized to 9.31 MPa and equilibrated for 10 min before the extraction commenced. Liquid CO₂ entered the precooler and passed through the hexane/SBO mixture and up through the column. The hexane-loaded L-CO₂ flowed out the top of the column across a micrometering valve and into a tared 100-mL round-bottom flask (cooled by an acetone/dry ice bath) to collect the extracted hexane and coextracted SBO. The expanded CO₂ exited at a flow rate of ca. 3–4 L/min (STP) through a dry gas test meter (model DTM-200A, American Meter Corp., Philadelphia, PA) used to measure the total volume of the CO₂ gas stream before it was vented to the atmosphere. Three hundred liters of CO₂ (STP) were used to perform each extraction. After each extraction, the column was cleaned to prevent contaminants from being carried over to subsequent runs. With the refrigerated circulating bath turned off, the column was heated to 100 °C and 800 L (STP) of SC-CO₂ (58.6 MPa) was passed through the column at 5 L/min.

Binary Gas Mixing Apparatus. The tendency of binary fluid pairs toward miscibility or phase separation has been discussed in detail (19, 20) and can be qualitatively predicted by a cohesive energy density approach (21). Although both N₂ and Ar are predicted to be miscible with CO₂ and He is predicted to be immiscible, experimental measurements have shown there is a finite solubility of He in CO₂, with the concentration of He in CO₂ proportional to both temperature and pressure (22, 23). At 25 °C and 8.1 MPa, the concentration of He in CO₂ has been estimated to be ca. 3 mol % (ca. 3.03 vol %) (24). Because of the relatively limited solubility of He in CO₂, only relatively low concentrations of He in CO₂ could be tested. The four concentrations of He in CO₂ mixtures tested were 0.5, 1, 2, and 4 vol % and were compared to neat CO₂. To obtain the He/CO₂ mixtures, individual gas flows were electronically controlled using Brooks Instruments

(Hatfield, PA) mass flow controllers. These gases were combined in a 2-L Parr Instrument (Moline, IL) stirred pressure reaction vessel held at 25 °C and ca. 2.1 MPa to produce the binary mixtures. The binary mixture was pressurized to 9.31 MPa using a gas booster pump (model AGT 62/152, Haskel International Inc.). Because N₂ and Ar are both miscible with CO₂, higher concentrations of these gases could be tested than with He. Four concentrations of N₂ and Ar in CO₂ mixtures (i.e., 1, 3, 10, and 30 vol %) were compared to neat CO₂.

The N₂/CO₂ and Ar/CO₂ binary gas mixtures were produced as described for He, except Sierra Instruments (Monterey, CA) mass flow controllers were utilized. For each gas tested, there were two replications at each binary gas concentration.

Collected and Raffinate SBO. A gentle stream of N₂ at 70 °C was used to remove the hexane from the collected SBO (i.e., extract) to a constant weight. The SBO extract masses for the various concentrations of each gas were recorded and analyzed separately to find mathematical equations that described the SBO mass collected (milligrams) versus binary gas concentration (volume percent) data using TableCurve 2D curve-fitting software (Systat Software Inc., Richmond, CA). The slopes and intercepts of the equations were compared after least-squares regression analysis using Statistix 7 software (Analytical Software, Tallahassee, FL).

The SBO raffinate was removed from the bottom of the column through the valve system and immediately placed in vials filled to the rim to prevent hexane loss through evaporation. Residual hexane levels in the SBO raffinate were determined by headspace GC analysis using ISO method 9832:2002 (18). The residual hexane levels for the various concentrations of each gas were recorded and analyzed separately to find mathematical equations that described the residual hexane concentration (parts per million) versus binary gas concentration (volume percent) data using TableCurve 2D curve-fitting software (Systat Software Inc.). The slopes and intercepts of the equations were compared after least-squares regression analysis using Statistix 7 software (Analytical Software).

Fatty Acid Compositional Analysis. Because previous research has shown that neat CO₂ extraction has a small effect on the fatty acid composition of both the extracted and raffinate SBO (4), potential effects of the binary gases mixed with CO₂ on fatty acid composition were investigated as well. For all concentrations of N₂ and Ar used, the fatty acid profiles were determined for the SBO carried over with the CO₂ and hexane (i.e., extract) and for the SBO left in the column (i.e., raffinate). One hundred milligram SBO samples were transesterified and analyzed by gas chromatography (GC) as described previously (25). A single GC analysis was performed on each sample. Analyses of variance (ANOVA) were conducted on the fatty acid percentage data using Statistix 7 software (Analytical Software).

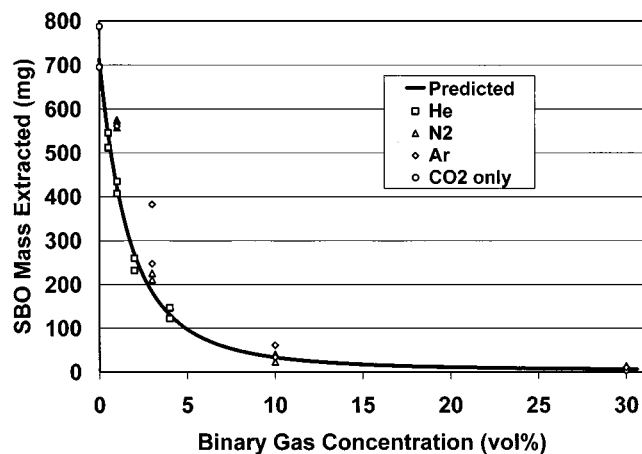


Figure 2. Soybean oil mass (milligrams) recovered from exiting CO₂ (300 L STP) as a function of volume percentage binary gas in CO₂ used to extract 42.2 g of a 25 wt % hexane/soybean oil mixture.

RESULTS AND DISCUSSION

The masses of coextracted SBO triglycerides as a function of percentage binary gas in CO₂ are shown in **Figure 2**. The amounts of SBO coextracted with the hexane were very similar for all binary mixtures, and all gas mixtures gave SBO masses that were inversely proportional to the binary gas concentration. The regression analysis of the SBO mass data (ln transformed) indicated that there were no significant differences between the slopes and intercepts ($F_{4,24} = 1.33$, $P = 0.29$) of the regression equations for the three binary gas types (i.e., He, N₂, and Ar) on the amount of SBO coextracted with the hexane. Therefore, the data for the three gas types were combined, and a single regression equation relating gas concentration to the amount of SBO coextracted was obtained. Both the slope and intercept of this regression were highly significant ($P < 0.00001$). Using the curve-fitting software, a relatively simple equation was found, which fit the SBO mass versus volume percent binary gas (VP) (all three gases) data very well: (mg of SBO) = $\exp[-1/(0.15224 + 0.01327 \times \text{VP})]$, with an R^2 value of 0.974. The predicted line is shown in **Figure 2**.

Although the mass of SBO coextracted was not completely suppressed, it was decreased from ca. 740 mg with neat CO₂ to ca. 134 mg when 4% He/CO₂ was used. This represents a >80% reduction in the carry-over of SBO coextracted with the hexane. This decrease in SBO solubility is very similar to the 70% reduction in SBO solubility previously reported using HHP-CO₂ to extract SBO from soybean flakes (14). Previous studies have investigated the solubilities of SBO and cholesterol He/CO₂ binary mixtures (15). Although the solubilities of both SBO and cholesterol are proportional to the density of the binary mixture and the density of the mixture is inversely proportional to the concentration of He in the CO₂, the differences in solvating capacities between pure CO₂ and binary mixtures cannot be fully explained by differences in their densities alone (15). At least part of this effect can be explained by the solvating power of the CO₂ being decreased when it is mixed with a cosolvent with a critical temperature lower than that of CO₂ (e.g., He, N₂, or Ar) (16), and this effect has been rationalized by the rules of Brunner (26). An increase in solubility in SC-CO₂ with polar liquid cosolvents (e.g., methanol, ethanol, or acetone) has been attributed to "clustering" effects or specific solute-cosolvent interactions in these mixtures (27, 28). Conversely, a reduction in solubility with gaseous cosolvents (e.g., He, N₂, or Ar) is related to the disruption of the CO₂ clustering around the solute molecules (29). The decreased

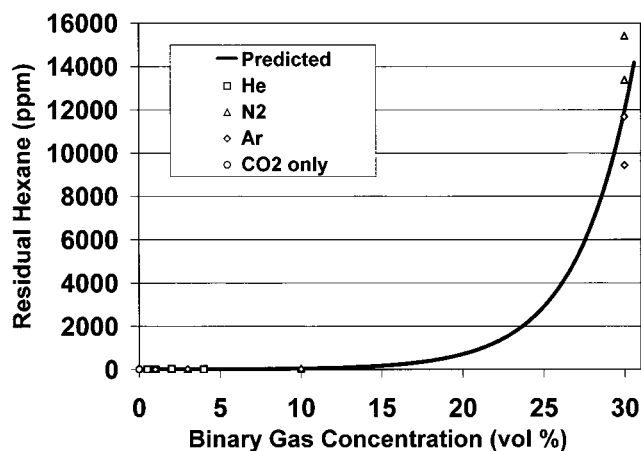


Figure 3. Residual hexane (parts per million) in raffinate soybean oil as a function of volume percentage binary gas in CO₂ (300 L STP) used to extract 42.2 g of a 25 wt % hexane/soybean oil mixture.

solubility of SBO observed with the binary mixtures of CO₂ is probably a result of the gaseous cosolvents (e.g., He, N₂, or Ar) disrupting the clustering of the CO₂ molecules around the SBO molecules and thus decreasing the CO₂'s ability to solvate the SBO molecules.

The mean residual *n*-hexane concentrations (parts per million) in the raffinate SBO extracted by the binary mixtures are shown in **Figure 3**. Again, the regression analysis of the residual hexane data indicated that there were no significant differences between the slopes and intercepts ($F_{4,19} = 0.85$, $P = 0.51$) of the regression equations for the three binary gas types (i.e., He, N₂, or Ar) on the residual hexane levels. Therefore, the data for the three gas types were combined, and a single regression equation relating gas concentration to the residual hexane level was obtained. Both the slope and intercept of this regression were highly significant ($P < 0.00001$). Using the curve-fitting software, a relatively simple equation was found, which fit the residual hexane concentration (C in parts per million) versus volume percent binary gas (VP) (all three gases) data very well: $\ln C = 0.894404 + (0.28317 \times \text{VP})$, with an R^2 value of 0.960. The predicted line is shown in **Figure 3**.

The residual hexane levels were extremely low for all concentrations up to ca. 10% binary gas in CO₂. Binary gas concentrations of 10% gave residual hexane levels that were very low (i.e., <40 ppm) and ca. 4% of what is typically achieved after the first stage of a conventional stripper (i.e., ca. 1000 ppm) (30). When the binary gas concentration was raised to 30%, the residual concentrations were quite high (i.e., >10000 ppm). However, even this relatively high residual hexane concentration still represents an approximately 96% reduction in hexane concentration from the original 250000 ppm (i.e., 25%) starting solution. Comparison of **Figures 2** and **3** indicates that the two lines intersect at ca. 10%. The 10% N₂/CO₂ and Ar/CO₂ binary mixtures appear to be an excellent compromise on both the removal of the hexane and the limitation of the coextraction of the SBO. With the 10% binary mixture, the residual hexane level was only 26 ppm and the SBO carry-over was only 40 mg. This 40 mg of SBO in the extract is only 0.13% of the original amount of SBO (i.e., 31.65 g) that was placed in the column, which means 99.87% remained in the raffinate. When neat CO₂ was used, the residual hexane level was 2.5 ppm and the SBO carry-over was ca. 741 mg, which represents over 2% of the SBO originally placed in the column. The 10% binary mixtures decreased SBO carry-over by ca. 95% from 741 mg to 40 mg while increasing residual hexane levels

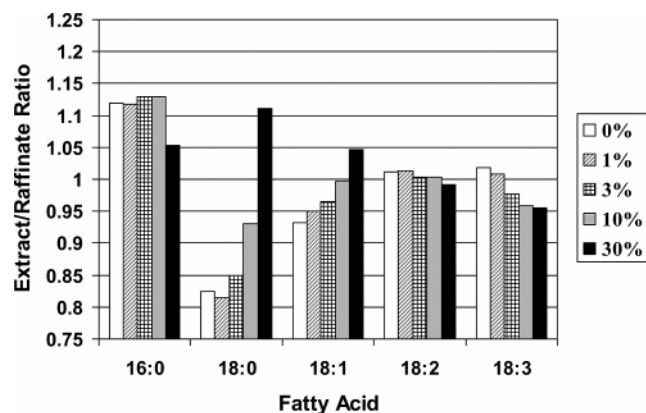


Figure 4. Ratios of extract/raffinate fatty acid composition as a function of volume percentage binary gas (nitrogen and argon) in CO₂.

only from 2.5 to 26 ppm when compared to neat CO₂. This represents an 18.5-fold reduction in SBO carry-over, and the residual hexane increased only ca. 10-fold using the 10% binary mixture. The disrupting effect of the gases added to the CO₂ appears to be less drastic for hexane than for the SBO. The disruption of the clustering of the CO₂ molecules by the gaseous cosolvents may be greater for the relatively large SBO molecules (e.g., MW of trilinolein = 880) (31) than for the relatively small hexane molecules (MW = 86).

The percentages of the five main fatty acids present in SBO (i.e., palmitic, 16:0; stearic, 18:0; oleic, 18:1; linoleic, 18:2; and linolenic, 18:3) were expressed as a ratio of those in the extract over those in the raffinate (extract/raffinate) for each fatty acid and the concentrations of nitrogen or argon tested (Figure 4). A ratio of >1 means the percentage of a given fatty acid was higher in the extract than in the raffinate. Conversely, ratios of <1 mean the percentage of a given fatty acid was higher in the raffinate than in the extract. The ANOVA of these ratios indicated there were significant main effects of fatty acid ($F_{4,66} = 287.9$, $P < 0.0001$) and gas concentration ($F_{4,66} = 26.5$, $P < 0.0001$), whereas the main effect of gas type (i.e., N₂ versus Ar) was not significant ($F_{1,66} = 0.00$, $P = 0.98$). The fatty acid \times concentration interaction was also significant ($F_{16,66} = 44.3$, $P < 0.0001$). Because the main effect for gas type was insignificant, the data for the two gases were combined and the data presented are an average of the two replications of the two gases (i.e., $n = 4$). The slight differences in the fatty acid compositions between the extract and raffinate after extraction of SBO with neat CO₂ seen in this study are virtually identical to those reported previously using neat CO₂ (4). Because the triglycerides making up SBO do not vary a great deal in their molecular weights (e.g., 807 for tripalmitin and 891 for tristearin) (31), one would not expect a great deal of differences in their relative solubilities in neat CO₂ or binary gas mixtures. Binary gas concentrations of 1, 3, or 10% behaved essentially like neat CO₂, and there were only very minor changes in the fatty acid compositions of either the extract or raffinate. The raffinate was enriched slightly in oleic acid (e.g., from ca. 21.5% to ca. 21.7%), whereas linoleic and linolenic acids were decreased slightly (e.g., from ca. 52.4 to 52.1% and ca. 6.9 to 6.5%, respectively).

Regression analyses were performed on the combined gas data to determine if there were significant effects of binary gas concentration on the extract/raffinate ratios. For the main fatty acids in SBO (i.e., palmitic, stearic, oleic, linoleic, and linolenic), the regressions were all significant ($F_{1,18} = 21.5$, $P = 0.0002$; $F_{1,18} = 184.8$, $P = 0.0000$; $F_{1,18} = 138.8$, $P = 0.0000$; $F_{1,18} = 14.1$, $P = 0.0015$; and $F_{1,18} = 10.7$, $P = 0.0043$, respectively).

The slopes of the equations were positive (i.e., the extract/raffinate ratio increases with increased binary gas concentration) for stearic and oleic acids, whereas the slopes of the equations were negative (i.e., the extract/raffinate ratio decreases with increased binary gas concentration) for palmitic, linoleic, and linolenic acids, although the magnitudes of the slopes were quite small.

This research demonstrates that the solvating properties of CO₂ can be significantly affected by the addition of relatively low amounts of a binary gas such as He, N₂, or Ar. When added to the CO₂, these three gases all affected the SBO solubility as well as the residual hexane in a similar manner. A single regression equation, applicable to He, N₂, or Ar, was derived to relate the binary gas concentration to the SBO mass extracted. Similarly, a single regression equation, applicable to He, N₂, or Ar, was derived to relate the binary gas concentration to the residual hexane concentration. The binary mixtures had a greater effect on the solubility of the SBO than on the solubility of the hexane when compared to neat CO₂ and led to an enhanced selective extraction of the hexane from the hexane/SBO mixture. This enhanced selectivity of binary mixtures of CO₂ may be applicable to other complex mixtures and may broaden the range of CO₂ extraction/reaction applications. Although this work was done in semibatch mode (oil in batch mode and CO₂ in continuous mode), to increase the practical application of the process, the fractionation column could be converted to run in continuous countercurrent mode.

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