

Fractionation of Lipids in a Static Mixer and Packed Column Using Supercritical Carbon Dioxide

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Fractionation of shark liver oil and olive oil deodorizer distillate using supercritical carbon dioxide was carried out in a laboratory-scale static mixer and laboratory- and pilot-scale packed columns. Both lipid mixtures contain squalene, which was the desired end product. The separation factor for squalene from shark liver oil was high, and the laboratory-scale packed column gave a degree of separation superior to that of the static mixer. The mass transfer performance of the static mixer was similar to that of the pilot-scale packed column for the recovery of squalene from olive oil deodorizer distillate. The separation factor for squalene was low, and more than one processing step was required before high purity squalene could be obtained. The pressure drop over the static mixer was measured and correlated against the specific energy consumption. For all operating conditions, the pressure drop was less than 1 bar and, hence, not significant for industrial-scale plant design. Literature correlations for drop size and overall mass transfer coefficients were compared with experimentally determined overall mass transfer coefficients. The correlation predictions agreed with experimental results only at low dispersed phase velocities in the static mixer.

Introduction

The continuous fractionation of lipids using supercritical carbon dioxide is of potential commercial interest for the production of nutraceutical and pharmaceutical products. Supercritical extraction, fractionation, and solubility studies have already been performed on a variety of lipids to isolate squalene,^{1–4} diacylglycerol ethers,^{1,2} carotenes,^{5,6} polyunsaturated fatty acids,⁷ lecithin,^{8,9} and vitamins A,^{1,10} and E.¹¹ Solubility studies have also been performed for a range of fish oils^{12,13} and fat-soluble vitamins.¹⁴ Almost all research and development in this area has focused on packed columns to provide interfacial area for the mass transfer process.^{1–11,15} The use of a static mixer has not been investigated to date for the fractionation of lipids under supercritical conditions.

Static mixers are typically used in the blending of liquids and gas–liquid mixtures, as tubular heat exchangers to improve heat transfer, in catalytic reactions for which a short residence time is desirable, and for mass transfer operations at ambient conditions.¹⁶ Static mixers have some distinct advantages over packed columns for use at supercritical conditions. These include a substantially lower capital cost at a large scale of operation, no possibility of flooding even if there is a low density difference between the phases (although the settler after the mixer could be affected), short residence times, and minimal space requirements for location in an extraction plant. However, the co-current mass transfer performance is unknown, and the pressure drop required over the mixer to achieve mass transfer may be too high for practical use. Static mixers have been

used in supercritical fluids for other applications. These include the mixing of CO₂ with polymer or paint solutions in the Unicarb spray process;¹⁷ the mixing of powder coatings and additives with supercritical CO₂ to make fine, coated particles from a gas-saturated solution;¹⁸ and the removal of caffeine from supercritical carbon dioxide by water.¹⁹ The caffeine removal research has been the most detailed investigation of the use of a static mixer at supercritical conditions. The static mixer was proposed as an alternative to a countercurrent packed column, which is used on an industrial scale. CO₂ partially to fully saturated with caffeine was put into contact with water in a static mixer. Pressure drop, droplet size, and mass transfer measurements were made. The efficiency of caffeine mass transfer was found to be around 80–90% of the equilibrium literature solubility.

In this work, the fractionation of two lipid mixtures is carried out in a laboratory/pilot-scale static mixer and compared with that achieved in laboratory- and pilot-scale packed columns. The lipid mixtures selected were deep sea shark liver oil (SLO), for which a substantial amount of mass transfer data has already been published,^{1,2} and olive oil deodorizer distillate (OODD), for which packed column mass transfer data have been reported.⁴ New packed column measurements for both lipid mixtures were carried out in this work. In both cases, the desired component is squalene. The separation factor between squalene and the other major components (triglycerides and diacylglycerol ethers) of deep sea shark liver oil is high. The selectivity for squalene over the other major components, fatty acids and methyl esters, is low for OODD.⁴

Experimental Section

Apparatus and Method. The pilot-scale apparatus used to carry out countercurrent fractionation of olive oil deodorizer distillate in a packed column or co-current

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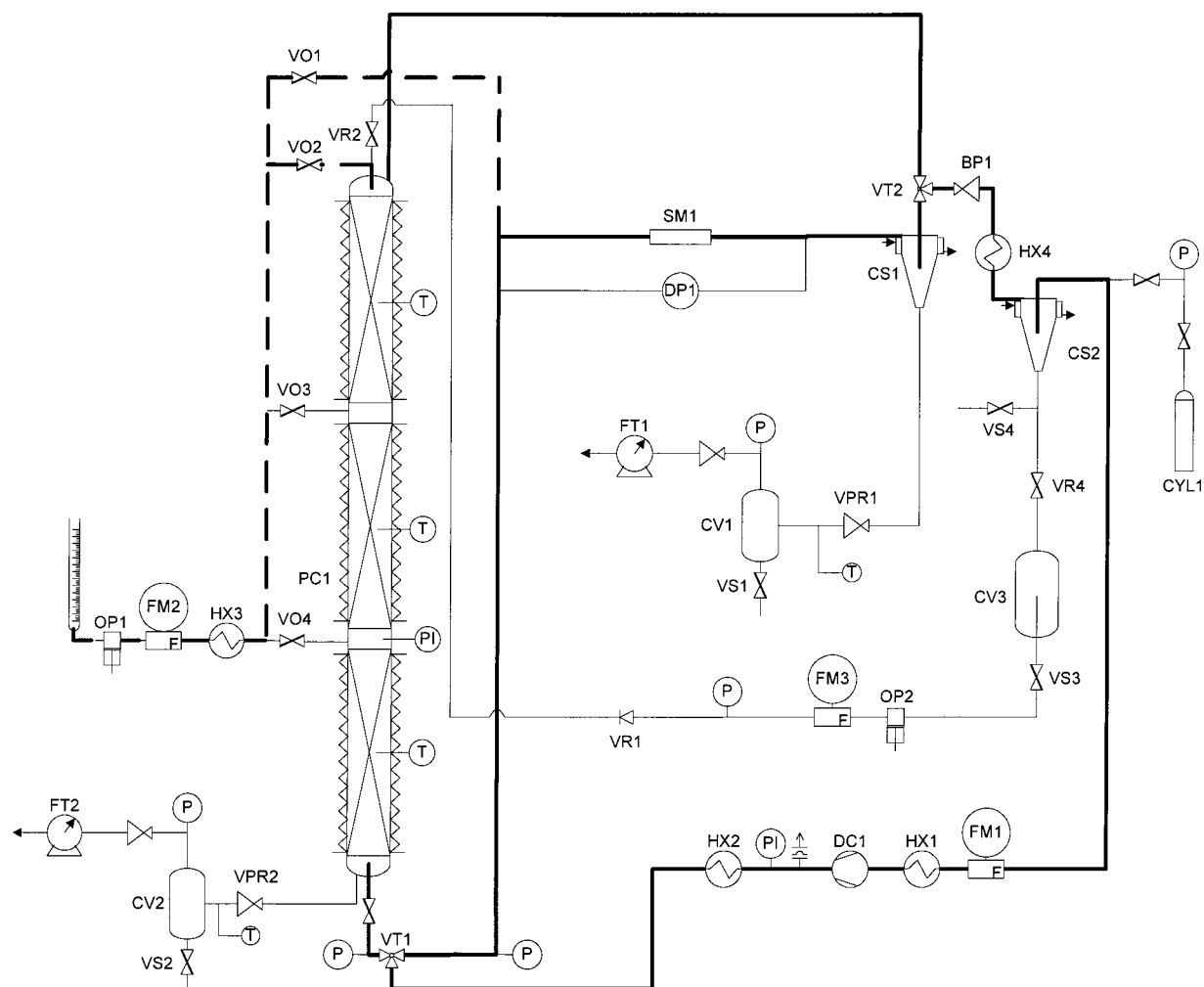


Figure 1. Schematic of pilot-scale packed column and static mixer apparatus.

fractionation in a static mixer is shown in Figure 1. The CO₂ flow path (shown as thick lines) for static mixer fractionation trials was around the loop containing flowmeter FM1, chiller HX1, diaphragm compressor DC1, preheater heat exchanger HX2, three-way valve VT1 (open to the right-hand side), static mixer SM1, cyclone separator CS1, three-way valve VT2 (open to the bottom branch), back-pressure regulator BP1, heater HX4, cyclone separator CS2 and back to FM1. The CO₂ flow path for packed column trials was around the loop FM1, HX1, DC1, HX2, VT1 (open to the left-hand side), packed column PC1, VT2 (open to the top branch), BP1, HX4, CS2, and back to FM1. Static mixer trials were carried out by bringing the apparatus to steady state with respect to CO₂ flow rate, fractionation and separation temperatures and pressures and then introducing oil flow (path shown as dotted lines) to the apparatus via diaphragm pump OP1, flowmeter FM2, preheater HX3, and inlet valve VO1. The CO₂ and lipid were put into contact in a tee joint just prior to SM1 and then passed isothermally and isobarically through SM1 and cyclonic separator CS1. Meter DP1 measured differential pressure across the static mixer and tee joint. SM1 and DP1 were both aligned in the horizontal plane to avoid any possible pressure head due to density and temperature differences.¹⁹ Raffinate was precipitated and collected at regular time intervals through valve VPR2 and into low-pressure receiver CV2 (maintained at 20 bar). The temperature of the oil as it passed through VPR1 was monitored. VPR1 was shut as soon

as a rapid decrease was observed. The CO₂ flashed from the oil at a constant receiver pressure was measured via flow totalizer FT1 and compared with the mass of oil recovered to determine the concentration of CO₂ in the lipid phase. Extract was recovered from cyclonic separator CS2 (maintained at the cylinder pressure) through valve VS4 at regular time intervals. Extract-free vapor-phase CO₂ was then recirculated back to the compressor via chiller HX1 to complete the cycle.

Packed column fractionation experiments were also started after steady state with respect to CO₂ flow rates, temperatures and pressures had been achieved. Oil was introduced to the packed column via pump OP1, FM2, HX3, and inlet valve VO2 or VO4. CO₂ passed upward through the column and the oil downward to enable countercurrent fractionation. Raffinate was collected from the bottom of PC1 through valve VPR2 (and from low-pressure receiver CV2) at regular time intervals by the same method used for the collection of raffinate from cyclonic separator CS1. Extract was recovered from CS2 as before. Reflux was carried out when required by using extract obtained directly from the second cyclonic separator vessel CS2, valve VR4, and reservoir CV3. The extract, at cylinder pressure, was fed to piston pump OP2 and compressed to the operating pressure. Flow rate, flow total, and density were recorded by flow meter FM3. The reflux then passed through valve VR2 to the top of column PC1.

The static mixer had an internal diameter of 4.6 mm, length of 220 mm, and 27 helical mixer stages. The

packed column internal diameter was 40 mm. The column was made up of three temperature-controlled sections that were 2, 1, and 1 m long from the base to the top, respectively. At the junction of each section and at the top and bottom of the column were sapphire windows for observing the flow of liquids in the column. Sulzer type EX structured packing with an interfacial area of $1710 \text{ m}^2 \text{ m}^{-3}$ and a hydraulic diameter of 1.886 mm was used as the column internals. The diaphragm compressor DC1, oil pump OP1, and reflux pump OP2 had mass flow capacities of 15, 6, and 4 kg h^{-1} , respectively.

The fractionation of shark liver oil has been carried out in other laboratory- and pilot-scale packed column supercritical fractionation plants that have been described elsewhere.^{1,2,12,13} Both apparatuses were modified to enable the use of the static mixer in place of the extraction column. In each case, the feed liquid and CO_2 were mixed in a tee joint just prior to the static mixer rather than at the top and bottom of the packed column, respectively. The outlet of the static mixer was connected directly to a high-pressure separator. The gas outlet from the separator then reconnected with the existing apparatus, which consisted of two separation vessels operated in a pressure-cascade mode, and then vented to the atmosphere (laboratory-scale) or recirculated back to a compressor (pilot-scale). The rates of oil and CO_2 feed, extract and raffinate mass flow rates, and extract and raffinate compositions were measured at a fixed fractionation temperature of 333 K and a pressure of 250 bar.

Materials and Analysis. Carbon dioxide was supplied by Air Liquide (instrument grade, 99.9% purity) in Portugal and BOC (industrial grade, 99.5% purity) in New Zealand. Olive oil deodorizer distillate was supplied by Fabrica Torrejana de Azeites, Portugal. The OODD was a complex mixture containing around 27% by mass squalene, 38% free fatty acids, and 35% other components including fatty esters (~1%), partial glycerides, sterols and sterol esters, tocopherols and hydrocarbons. The shark liver oil was supplied by MacCure Seafoods, New Zealand. It contained around 55% squalene, 0.15% pristane, and 45% mixed triglycerides and diacylglycerol ethers. Analysis of OODD fractions for squalene, fatty acid esters, sterols, sterol esters, and free fatty acids was carried out by GC. Total free fatty acids were also determined by titration. Squalene and pristane contents of SLO fractions were determined by GC. The squalene content was also determined by refractive index.

Correlation of Static Mixer Mass Transfer Coefficients

The mass transfer performance of continuous contact devices is usually evaluated in terms of the number of transfer units, NTU, and the height of a transfer unit, HTU through

$$Z = \text{HTU} \times \text{NTU} \quad (1)$$

with

$$\text{NTU} = \int_{C_{\text{in}}}^{C_{\text{out}}} \frac{dC}{C - C^*} \quad (2)$$

$$\text{HTU} = \frac{U_d}{k_{\text{od}} a} \quad (3)$$

For static mixers, the NTU has been approximated by^{20,21}

$$\text{NTU} = \frac{C_{\text{in}} - C_{\text{out}}}{(C - C^*)_{\text{in}} - (C - C^*)_{\text{out}}} \ln \left[\frac{(C - C^*)_{\text{in}}}{(C - C^*)_{\text{out}}} \right] \quad (4)$$

Mass transfer correlations for Sulzer-type static mixers have been presented in the literature in terms of the specific energy usage, E_v .²² The measured pressure differential over the static mixer was correlated against E_v , according to the following equations:²²

$$E_v = \frac{\Delta P U_c}{\rho L \epsilon} \quad (5)$$

$$E_v = \frac{f U_c^3}{2 \epsilon^3 D_h} \quad (6)$$

A plot of E_v versus $U^3/2\epsilon^3 D_h$ yields the friction factor f . The drop diameter can be estimated from an equation based on the specific energy usage, which has been derived for Sulzer static mixers.²²

$$d_{\text{sv}} = 0.65(1 + 3\varphi_d) \left[\frac{(1 + BVi) We_c}{2} \right]^{0.6} \left(\frac{\sigma}{\rho_c} \right)^{0.6} \left(\frac{\rho_c}{\rho_d} \right) E_v^{-0.4} \quad (7)$$

Although the mixer used in this work is not a Sulzer mixer, the correlation should give a reasonable estimate of the droplet diameter, as it was based on three types of mixers with different internals and a variety of test fluids. The viscosity number, Vi , and density correction terms are small, giving d_{sv} proportional to $(\sigma/\rho_c)^{0.6} E_v^{-0.4}$. For lipid/ CO_2 systems, the interfacial tension is strongly dependent on temperature and pressure. At fixed temperature, the interfacial tension of lipid/ CO_2 saturated mixtures decreases asymptotically toward zero as the pressure increases.²³ Mass transfer is thus favored at high pressures as the interfacial tension is low and the continuous-phase density is high. A two-film model is proposed for mass transfer from the dispersed (lipid) phase to the continuous (CO_2) phase.

$$\frac{1}{k_{\text{od}} a} = \frac{1}{k_d a} + \frac{m}{k_c a} \quad (8)$$

A correlation based on mass transfer measurements in Sulzer mixers²² and converted to dimensionless numbers has been applied for the continuous phase for this work.

$$k_c a = 0.198 a \left(\frac{D_c}{d_{\text{sv}}} \right) (\text{Re}_c \text{Sc}_c)^{0.5} \quad (9)$$

The drop size is expected to be small ($<1 \text{ mm}$). The droplet is stationary with respect to the continuous phase as the residence time of both phases is the same. Wesselingh and Bollen²⁴ suggest that the mass transfer coefficient can be predicted for small droplets in the dispersed phase by the dimensionless correlation $\text{Sh}_d = 10$, whereas Pietch and Eggers¹⁹ used $\text{Sh}_d = 2$. The droplet interfacial area per unit volume was estimated from eq 10 as^{20,21}

$$a = \frac{6\varphi_d}{d_{\text{sv}}} \quad (10)$$

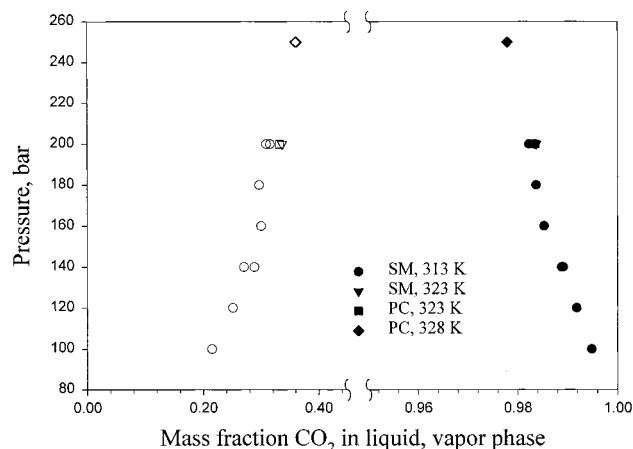


Figure 2. Mass fraction of CO₂ in the liquid and vapor phase versus pressure for selected static mixer and packed column trials. Hollow symbols, liquid phase; solid symbols, vapor phase. *S* at 313 K and 140, 200 bar = 13.5, 25.2 g kg⁻¹, respectively; at 200 bar and 323, 328 K = 23.8, 22.3 g kg⁻¹, respectively; and at 250 bar, 328 K = 35.8 g kg⁻¹.

Combination of eq 10 with $Sh_d = 2$ gives the drop-phase mass transfer coefficient as

$$k_d a = 12 \frac{\varphi_d D_d}{d_{sv}^2} \quad (11)$$

The viscosities, phase densities, diffusion coefficients, and surface tensions required in the correlation equations were estimated as outlined in previous work.² The following values were used in the estimation of mass transfer coefficients for the shark liver oil/CO₂ system: $\rho_d = 860 \text{ kg m}^{-3}$, $\rho_c = 787 \text{ kg m}^{-3}$, $\eta_d = 8.10 \times 10^{-4} \text{ N s m}^{-2}$, $\eta_c = 6.78 \times 10^{-5} \text{ N s m}^{-2}$, $D_d = 1.42 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_c = 5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $S = 34.8 \times 10^{-3} \text{ kg kg}^{-1}$, $\sigma = 1.0 \times 10^{-3} \text{ N m}^{-1}$, and $K(\text{squalene}) = 0.0361$.

Results and Discussion

Olive Oil Deodorizer Distillate. Fractionation of olive oil deodorizer distillate (OODD) was carried out to demonstrate the separation performance of the static mixer and packed column for recovering squalene from a system in which the achievable separation is low.⁴ The OODD used in this work differed from that used in previous work,^{3,4} and so the experimental trials focused on phase equilibrium and the effect of process variables on the degree of separation. OODD was fractionated in the static mixer over the pressure range 100–250 bar, the temperature range 313–333 K, and the oil-to-CO₂ flow rate ratio range 0.014–0.043. Packed column trials were performed over the pressure range 160–250 bar, the temperature range 313–333 K, and the oil-to-CO₂ flow rate ratio range 0.035–0.075. The fractionation experiments yielded information on the pressure drop over the static mixer; the solubilities of the oil in CO₂ and of CO₂ in the oil, the composition of the phases (and especially the squalene content); and the distribution coefficients for the three key components squalene, fatty acids, and fatty acid esters.

The mass fraction of CO₂ in the extract phase at high oil-to-CO₂ ratios, and the corresponding CO₂ solubility in the lipid phase, is shown as a function of pressure in Figure 2 for selected static mixer and packed column trials. The solubility increases markedly with pressure, while the CO₂ solubility increases slowly. At fixed

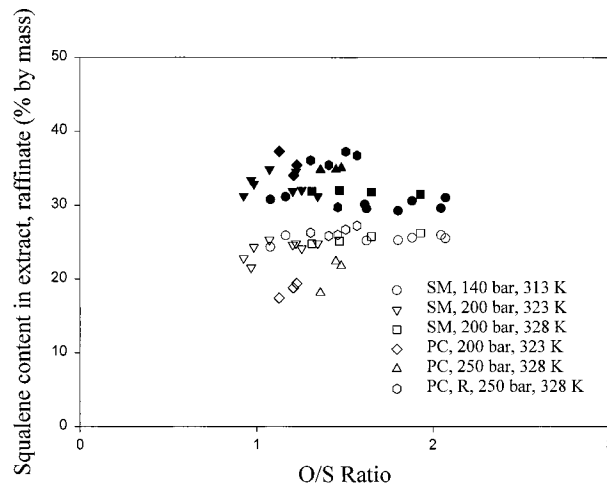


Figure 3. Squalene concentration in extract (solid symbols) and raffinate (hollow symbols) as a function of the *O/S* ratio for selected static mixer and packed column trials.

temperature and pressure, the solubility increases asymptotically to a fixed value with increasing *L/G* ratio (see below) in a manner similar to that observed for shark liver oil.² The solubility figures used in Figure 2 were from experiments with high *L/G* ratios. In contrast, the solubility of CO₂ in the lipid phase was almost independent of the *L/G* ratio. Agreement between the packed column and static mixer is reasonable for the overlapping conditions measured. The static mixer should be equivalent to one theoretical stage of separation due to co-current operation. The static mixer and settler may be a useful way to rapidly obtain single-component phase equilibrium data. Steady state is rapidly achieved, and the residence time in the mixer is very short. The solubility at fixed temperature and varying pressure can be established more rapidly than in stirred autoclave trials.

The extracts obtained from both packed column and static mixer trials were of low viscosity and strongly scented, and they contained a small amount of water from the prior distillation step. The raffinate samples were generally darkly colored, viscous, and weakly scented, with no apparent water. Fatty acid esters were concentrated in the extract, while partial glycerides, tocopherols, and sterols were concentrated in the raffinate. Squalene was slightly concentrated in the extract compared to the feed, and fatty acids were slightly concentrated in the raffinate. The concentration of squalene in the extract (determined by GC) as a function of the *O/S* ratio² defined by eq 12 is shown in Figure 3.

$$\frac{O}{S} = \frac{L}{GS} \quad (12)$$

where *S* is the solubility of squalene at the extraction temperature and pressure, which has been reported elsewhere,^{12,13} and is shown in the figure caption. This ratio was chosen to enable comparison with the extraction of squalene from shark liver oil.² At an *O/S* ratio greater than 1, the concentration of squalene in the extract was fixed within experimental error. Marginally higher squalene concentrations could be achieved with the packed column, but the degree of separation was very low. Reflux was not strongly beneficial when the packed column was used. The squalene concentration was slightly improved relative to trials in which no reflux was used, but the losses of squalene in the

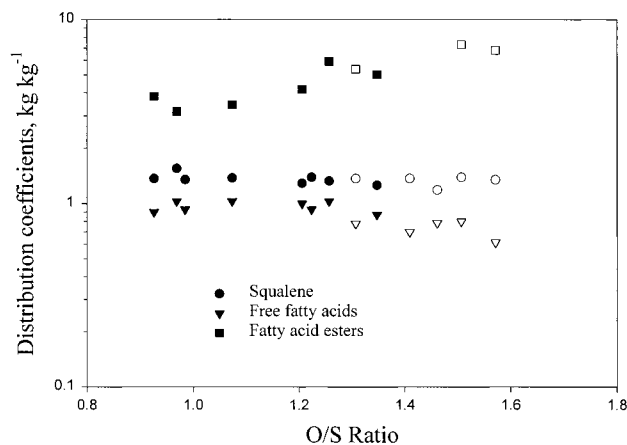


Figure 4. Distribution coefficients for fatty acid esters, squalene, and free fatty acids as a function of the O/S ratio for the static mixer at 200 bar and 323 K (solid symbols) and for the packed column at 250 bar and 333 K with reflux (hollow symbols).

raffinate increased to the same magnitude as for the case of the static mixer. The loading (apparent solubility of ODD in CO_2) also became constant at fixed temperature and pressure for O/S values greater than 1.

Distribution coefficients, K_i , (on a CO_2 -free mass basis) were determined for selected components by GC from extract and raffinate samples. The distribution coefficients for total fatty acid esters, squalene, and total free fatty acids are shown as a function of the O/S ratio for a static mixer trial at 200 bar, 323 K; and packed column trial at 250 bar and 333 K with reflux in Figure 4. The distribution coefficients for squalene are just greater than one, and those for the fatty acids are just less than or equal to 1, indicating poor separation between the two components. The pressure and temperature did not strongly affect the squalene and fatty acid concentrations in the extract over the ranges investigated. Fatty acid esters, being the most soluble components, had the highest distribution coefficients. These findings mirror those already reported for packed column countercurrent extraction of ODD, although the feed material used in this work had a much lower concentration of fatty acid esters.⁴ The poor degree of separation between squalene and fatty acids is similar to the findings reported for other lipid mixtures containing these components.^{25,26} To achieve high-purity squalene, several processing stages are required,⁴ or the ODD must be treated before extraction to remove the fatty acids or to convert them to less soluble lipids such as triglycerides.³ The distribution coefficient for squalene in the packed column (without reflux) was found to be higher than that in the static mixer, although only a limited number of trials were carried out for overlapping pressure and temperature conditions.

Shark Liver Oil. Fractionation of deep sea shark liver oil was carried out to demonstrate the separation performance of the static mixer and packed column for recovering squalene from a system in which the achievable separation is high.^{1,2} Phase equilibrium for the shark liver oil/ CO_2 and squalene/ CO_2 systems had already been established,^{12,13} and so the fractionation trials focused on scale-up and mass transfer aspects of the use of the static mixer at fixed temperature (333 K) and pressure (250 bar). Static mixer trials for recovering squalene from shark liver oil were carried out at both a laboratory scale (CO_2 mass flow rates up to 5 kg h^{-1}) and a pilot scale (mass flow rates to 12 kg h^{-1}). The

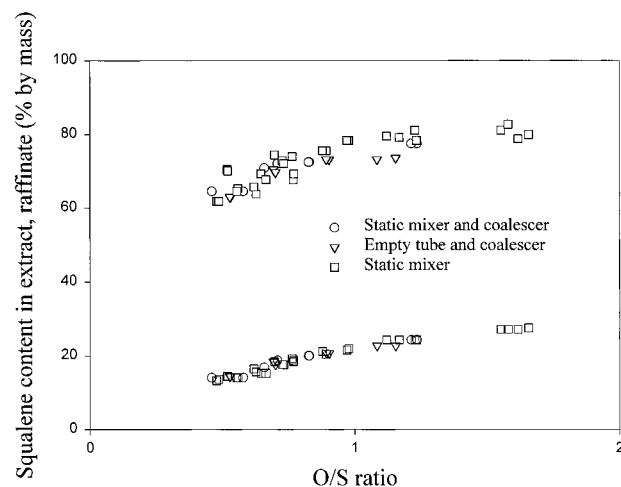


Figure 5. Squalene concentration in extract (top curve) and raffinate (bottom curve) as a function of the O/S ratio for laboratory-scale trials using a static mixer and coalescer, static mixer and downcomer tube, and an empty tube with coalescer.

configuration of the settler following the static mixer was also varied. Oil and CO_2 entered the settler through a vertical downcomer tube. Laboratory-scale trials were carried out using the tube and a coalescer filter and using a downcomer tube only. In addition, laboratory-scale trials were also carried out in which the static mixer was replaced by an empty tube (and a coalescer filter was used in the separator). The results of these trials are shown in Figure 5 as a function of the O/S ratio. Replacement of the static mixer with an empty tube resulted in a small decrease in fractionation performance. This suggests that the majority of the mass transfer was taking place in the tee joint prior to the mixer, where the fluids are initially brought into contact. There was no difference in extract and raffinate composition or yield between the static mixer trials with and without the coalescer filter. However, no trials were performed with the empty tube and downcomer tube only, and so the coalescer filter may have had some beneficial effect. The ratio of oil to CO_2 and the CO_2 flow rate were varied to establish the influence of these parameters on the degree of extraction of squalene. The ratio of oil to carbon dioxide was the most important parameter. At a fixed oil-to- CO_2 ratio, changes in the CO_2 (and oil) flow rates had no effect on the extract and raffinate compositions.

The extract and raffinate squalene concentrations as functions of the O/S ratio are shown in Figure 6 for laboratory- and pilot-scale flow conditions. For laboratory scale, the CO_2 flow rate was varied in the range $1.29\text{--}4.71 \text{ kg h}^{-1}$. At a pilot scale, the range covered the range $7.38\text{--}12.50 \text{ kg h}^{-1}$. There is no difference within experimental error between the two series of results over an almost 10-fold variation in mass flow rate. Also included in Figure 6 are the squalene extract and raffinate concentrations from laboratory-scale packed column trials carried out at the same shark liver oil, extraction oil, temperature, pressure, and oil-to- CO_2 flow rate ratio range. There is a clear improvement in the degree of separation between squalene and the other components of shark liver oil and a corresponding increase in the solvent capacity of the CO_2 (loading). This is not an unexpected result, as the packed column operates in a countercurrent mode and provides a number of theoretical separation stages, whereas the

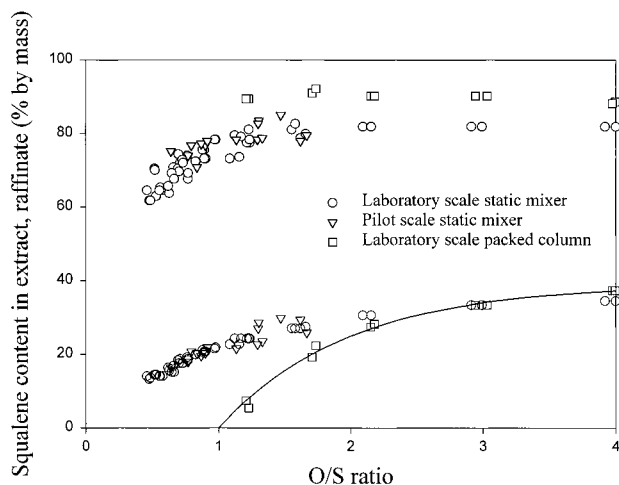


Figure 6. Squalene concentration in extract (top curves) and raffinate (bottom curves) as a function of the O/S ratio for laboratory- and pilot-scale static mixer trials and laboratory-scale packed column trials. Solid curve: $C^* = 39.1\{1 - \exp[-1.017(O/S - 1)]\}$.

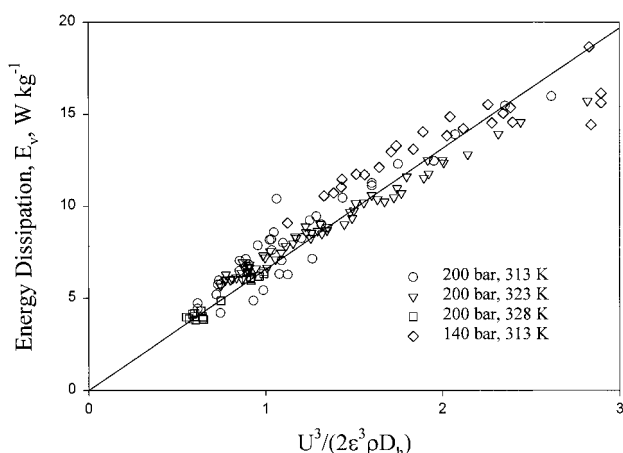


Figure 7. Energy dissipation as a function of (superficial velocity)³/geometric factor at four temperature and pressure combinations.

static mixer is co-current and provides only one theoretical stage.

Correlation of Mass Transfer Coefficients. Mass transfer coefficients for the transfer of squalene from the dispersed phase to the continuous CO_2 phase were estimated at the fixed temperature of 333 K and the fixed pressure of 250 bar using the methodology outlined in the correlation section. Correlation of the experimentally determined mass transfer coefficients required the measurement of the pressure loss across the static mixer. The pressure loss was used to calculate the energy dissipation, E_v . E_v is shown as a function of the superficial velocity for four different pressure and temperature combinations and OODD-to- CO_2 mass flow rate ratios in Figure 7. The ratio of OODD to CO_2 had little influence on the measured pressure differential. The variation in E_v with U^3 was almost linear for all pressure and temperature combinations (except at high velocities where the limit of the meter was reached), enabling an average friction factor to be calculated. This friction factor was used to estimate drop diameters and mass transfer coefficients from eqs 7, 9, and 10, respectively.

Estimates of the overall mass transfer coefficient, $k_{od,a}$, were obtained from the experimentally determined

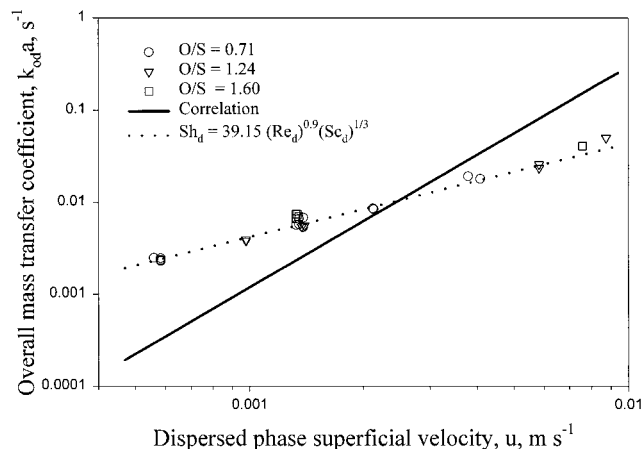


Figure 8. Overall mass transfer coefficient based on the dispersed phase versus dispersed phase superficial velocity: experimental results (three O/S ratios) and model predictions. Solid line is the correlation model; dotted line is a dimensionless correlation (this work).

NTU. The equilibrium concentration of squalene in the liquid phase, C^* , at a set O/S ratio was taken to be that achieved in the packed column. An empirical curve was fitted to the packed column squalene raffinate data to predict C^* at given O/S values for use in the calculation of the NTU. This curve is shown in Figure 6. The overall mass transfer coefficient based on the dispersed phase is shown as a function of the dispersed-phase superficial velocity with O/S as an additional parameter in Figure 8. The overall mass transfer coefficient increased monotonically with velocity at fixed O/S and increased with increasing O/S at fixed velocity although the data show considerable scatter. Also shown are the overall mass transfer coefficients predicted from the correlation model at an O/S ratio of 0.71 and a dimensionless correlation obtained from minimizing the error between the experimental and predicted data given below as eq 13.

$$Sh_d = 39.15 Re_d^{0.9} Sc_d^{1/3} \quad (13)$$

The agreement between the correlation model and the experimental results is poor. There are a number of possible reasons why the correlation method was not successful. An unknown extent of mass transfer takes place in the tee junction prior to the static mixer. The mass transfer due to mixing in the tee joint may be the dominant mass transfer mechanism at low superficial velocities, and it may then decrease in significance as the superficial velocity increases. The droplet sizes achieved experimentally may vary with superficial velocity due to the tee in a manner that is different from that predicted from the correlation. Finally, the mass transfer coefficient model for the drop phase may not be correct. The model is used when the drop is stationary with respect to the continuous phase. The model does not take account of drop breakup due to collisions with the mixer internals, coalescence and radial flow. The agreement between the purely empirical correlation and experimental results is good, but its applicability beyond the circumstances used in this work is not known.

Conclusions

The degree of separation that can be achieved with a static mixer is less than that achievable with a labora-

tory- or pilot-scale packed column for easily fractionated mixtures (shark liver oil) and is similar for difficult to fractionate mixtures (olive oil deodorizer distillate). Static mixer and settler systems have potential to be used for measuring the equilibrium solubility of single components in the fluid phase and of the fluid phase in the liquid. The pressure differential across the mixer was measured and found to be less than one bar over a 10-fold variation in mass flow rates. Overall mass transfer coefficients were measured and compared with predictions from a correlation model. The measured coefficients were lower than predicted except at low superficial velocities in the mixer. The reasons for the discrepancy between the model predictions and experimental results have not been ascertained. An empirical correlation was also developed in this work to fit the experimental data.

Nomenclature

a = droplet interfacial area per unit volume [m^2/m^3]
 B = drop diameter constant [1.3]
 C_{in} = inlet concentration [kg/m^3]
 C_{out} = outlet concentration [kg/m^3]
 C^* = equilibrium concentration [kg/m^3]
 D = diffusion coefficient [m^2/s]
 D_h = hydraulic diameter of the static mixer [m]
 d_{sv} = Sauter mean diameter of droplet [m]
 E_v = energy dissipation [W/kg]
 f = friction factor
 G = continuous-phase mass flux [$\text{kg}/\text{m}^2 \text{ s}$]
 HTU = height of a transfer unit [m]
 k = film mass transfer coefficient [m/s]
 k_{od} = overall mass transfer coefficient (eq 8) in the dispersed phase
 K = distribution coefficient on a mass basis [kg/kg]
 L = dispersed-phase mass flux [$\text{kg}/\text{m}^2 \text{ s}$]
 m = distribution coefficient [L/GK]
 NTU = number of transfer units
 O/S = ratio defined by eq 12
 ΔP = pressure differential over static mixer [bar]
 Sc = dispersed phase Schmidt number [$\eta/\rho D$]
 S = solubility of squalene in CO_2 [kg/kg]
 Sh = Sherwood number of dispersed phase [kd_{sv}/D]
 U = superficial velocity [m/s]
 Vi = viscosity number [$\eta_d(E_v d_{\text{sv}}/0.65)^{1/3}(\rho_c/\rho_d)^{1/2}/\sigma$]
 We_c = critical Weber number [taken to be 1.8]
 Z = length of static mixer [m]

Greek symbols

ϵ = void volume fraction of mixer
 φ_d = dispersed phase hold-up
 η = viscosity [$\text{N s}/\text{m}^2$]
 ρ = density [kg/m^3]
 σ = surface tension [N/m]

Subscripts

c = continuous phase
d = dispersed phase

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