Use of Adsorbent and Supercritical Carbon Dioxide To Concentrate Flavor Compounds from Orange Oil

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Orange oil is composed largely of terpene hydrocarbons but is a source of flavor and fragrance compounds (oxygenated) that are present in low concentrations. To increase the ratio of oxygenated compounds to terpene hydrocarbons, orange oil was partially fractionated by adsorption of the oxygenated compounds onto porous silica gel, with full utilization of its adsorbent capacity, and then further purified by desorption into supercritical carbon dioxide. The desorption of 24 compounds was monitored by GC and GC-MS. Adsorption alone removed three-fourths of the terpene hydrocarbons, and fractional extraction by supercritical carbon dioxide (SC-CO$_2$) improved the separation further. Response surface methodology was used in the experimental design, and regression analysis was used to determine the effects of process variables. Extraction at low temperatures and flow rates improved separation by SC-CO$_2$. Decanal was concentrated to 20 times that of the feed oil by using SC-CO$_2$ at 13.1 MPa, 35 °C, and 2 kg/h. The systems were operating at close to equilibrium conditions because of the fine dispersal of the oils and the excellent mass transfer properties of supercritical carbon dioxide.

INTRODUCTION

Orange oil is used by the food and pharmaceutical industries as a source of flavor and fragrance. It is composed of mainly terpene hydrocarbons and oxygenated compounds. Terpene hydrocarbons do not contribute to the flavor and fragrance of orange oil. They serve only as a flavor carrier for oxygenated compounds, which are present in low concentrations (*1*). The terpene hydrocarbons are unstable to heat and light and gradually taint the flavor and aroma of the oil during storage (*2*), making it unfit for flavor applications. Removal of terpene hydrocarbons, mainly D-limonene, by distillation, solvent extraction, supercritical fluid extraction, and adsorption, has been investigated to increase the concentration of oxygenated flavor compounds and to improve shelf stability and handling properties. Distillation is the most commonly used commercial method to increase the concentration of flavor compounds 10−20 times (10−20-fold) that of the original oil. Use of high temperatures during distillation is known to produce artifacts that reduce the quality of the concentrate (*2*).

Investigations into the use of adsorbents for refining citrus oil have been carried out for about half a century. These studies utilized adsorbents, such as silica gel, that selectively adsorb the polar compounds. The terpene compounds were removed with the aid of a nonpolar solvent, and concentrated oxygenated compounds were later eluted by more polar organic solvents or supercritical or liquid carbon dioxide. Loading ratios of oil to silica gel have been reported from 0.003 to 800% (*3*−*12*).

The adsorptive capacity of silica gel for orange oil has been compared with that of other adsorbents by Braverman and Solomiansky (*4*). A mixture of alumina and kieselguhr had the same adsorptive capacity as silica gel, based on the ratio of volume of oil adsorbed to the total volume of oil stripped of oxygenated compounds. For both adsorbents the ratio was 1:6 and, on a weight basis, the adsorptive capacity of silica gel was 3.2 g of oil/g of adsorbent (*4*). Ferrer and Matthews (*5*) found that the adsorptive capacity of Florisil was 2.2 g of oil/g of adsorbent, calculated as the maximum amount of oil added onto a column of the adsorbent that gave a negative test for aldehydes in the eluate. For silica gel, a loading ratio of oil to silica gel of 4.4 times was deemed the maximum adsorptive capacity. Tzamtzis et al. (*6*) reported a loading ratio (by weight) of 7.9. Yamauchi and Saito (*7*) showed that an advantage of using a lower oil-loading ratio, such as 20%, was the ability to separate components in lemon peel oil into different groups. Indeed, the

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loading ratio of oil to adsorbent to give a good separation is not well defined. The optimum loading ratio is principally determined by the capacity of the adsorbent for oxygenated compounds. Furthermore, the solvents used to subsequently elute the adsorbate can affect the degree of separation achieved by the process as a whole and therefore may affect the optimum loading ratio. More recently zeolites have been reported for the purification and separation of flavor-effective or fragrance molecules by adsorption (*13*).

Parallel to the above developments has been the use of silica gel chromatographic methods with supercritical carbon dioxide (SC-CO$_2$) as the solvent (*7, 9–11, 14, 15*) for semipreparative fractionation of citrus oils without utilizing the full adsorptive capacity of silica gel for oxygenated compounds. Chouchi et al. (*16*) reported the desorption curves of a model mixture containing six hydrocarbon terpenes and six oxygenated terpenes through silica gel and showed that at a higher SC-CO$_2$ density of ~0.75 g/cm^3 (37 °C, 13 MPa) all breakthrough curves overlapped and no selectivity was observed. However, at a lower CO$_2$ density of ~0.50 g/cm^3 (47 °C, 10 MPa) two different curve families were observed for hydrocarbons and oxygenated terpenes, respectively. The conclusion was drawn that the lower the density of CO$_2$, the better the selectivity that can be obtained.

The aim of the present work was to study the fractionation of orange oil by adsorption with full utilization of the adsorbent capacity, followed by desorption into SC-CO$_2$, and to identify conditions leading to higher yield and concentration of flavor compounds, using with response surface methodology.

MATERIALS AND METHODS

Materials. Silica gel 60 (3% moisture, 70–230 mesh) and aluminum oxide 90 (activity I, neutral, 70–230 mesh) with purity of column chromatography grade (Merck) were assessed as adsorbents. Cold-pressed navel orange oil (Auroma, batch Ausil 21062) from *Citrus sinensis*, 100% essential oil with a specific gravity of 0.812, was used for adsorbent assessment. Cold-pressed Valencia orange oil with a specific gravity of 0.842 used for SC-CO$_2$ desorption was generously supplied by Keith Harris & Co. Ltd. (Thornleigh, NSW, Australia).

Assessment of Adsorbents. Silica Gel 60 (14.9 g, weighed to 0.01 g accuracy and bed height ~14.3 cm) or Aluminum Oxide 90 (14.7 g, weighed to 0.01 g accuracy and bed height ~7.5 cm) were loosely packed into a chromatography column [17 mm (i.d.) × 20 cm]. Navel orange oil was pumped by HPLC pump (Bio-Rad Econo Pump) onto the top of the column at a rate of 0.96 g of oil/min. The stripped oil emerging from the bottom of the column was collected as fractions. There were between 11 and 15 fractions of ~5 g collected from each fractionation over 55–75 min. These fractions and the feed were analyzed by GC-MS (for compound identification) and GC (for quantification) or by GC only.

The loading ratio of oil to adsorbent (w/w) at the time of collection of each fraction was calculated as the ratio of the cumulative amount of orange oil pumped through the adsorbent column to the fixed amount of adsorbent. As the orange oil was pumped continuously, the loading ratio increased continuously.

Analysis Methods (GC and GC-MS). GC analyses were performed with a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector and a split injector operated at 270 and 220 °C, respectively. Separations were achieved on a J&W DB-5 capillary column (30 m × 0.32 mm i.d., film thickness of 0.25 μm). The following temperature programs were used: 60–240 °C at 3 °C/min for analyzing oxygenated compounds; 60–108 °C at 3 °C/min and further to 240 °C at 20 °C/min for analyzing limonene; a helium flow of 1.5 mL min^{-1} and split ratio of 20:1 or 60:1 for analyzing oxygenated compounds or limonene, respectively. All analyses were carried out in duplicate. The results were calculated on the basis of a normalization method (GC peak area percentage) for adsorbent assessment and by using an internal standard, durene (*10*), for SC-CO$_2$ desorption work.

Table 1. Primary Variables and the Levels Used for Full Factorial Experiment Design

P (MPa)	level code	T (°C)	level code	flow rate (kg/h)	level code
9.66	−1	35	−1	2	−1
13.10	−0.5238	45	0	4	1
24.14	1	55	1		

The response factors of limonene and decanal were used as the response factors for all terpene hydrocarbons and oxygenated compounds, respectively. Durene solution was made by dissolving ~1 g of durene, weighed to 0.1 mg accuracy, in 100 g of chloroform.

GC-MS analyses were conducted by a Varian GC 3400 directly coupled to the input of a Varian Saturn GC-MS, and mass spectra were produced using electron impact ionization. A split injection system and a J&W DB-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film) were used with a column helium flow rate of 1 mL min^{-1}. The GC oven temperature was increased from 60 to 240 °C at 3 °C/min (*17*). The other temperature settings were as follows: injector, 220 °C; manifold, 220 °C; and transfer line, 255 °C. Components were identified by the GC-MS spectrum library (Terpene Library, Varian Saturn GC-MS) combined with the elution order of terpene compounds on the DB-5 column (*17*) and comparison of their retention times with those of some authentic standards.

Layout and Operation of SC-CO$_2$ Desorption Plant. The layout of the SC-CO$_2$ plant was similar to the one described earlier (*18*). Silica Gel 60 (100 g) was dry packed into the extractor column, and Valencia orange oil (500 g ± 3%) was pumped by HPLC pump (Bio-Rad Econo Pump) onto the top of the silica gel at 2.8 g of oil/min for ~3 h, and the unadsorbed oil fraction passing through the silica gel was collected from the bottom of the column. After the free drainage of oil had stopped, the column was sealed, slowly pressurized with CO$_2$ to 3.45 MPa at room temperature, and slowly depressurized to atmospheric pressure to expel any oil fraction held in the void space of the silica gel bed. The column was then brought to the required pressure and temperature of SC-CO$_2$. The desorption by SC-CO$_2$ at specified pressure and temperature was continued for 2.5 h, and fractions were collected at the following times: 5, 10, 20, 30, 50, 70, 100, and 150 min (referred to as fractions 1, 2, 3, 4, 5, 6, 7, and 8, respectively). All fractions were weighed, and aliquots were subjected to GC and GC-MS or GC only. The adsorption was carried out essentially as described by Ferrer and Matthew (*5*), making full use of the adsorptive capacity of the adsorbent.

Experimental Design of SC-CO$_2$ Desorption. Some preliminary experiments for refining of Valencia oil with SC-CO$_2$ and silica gel in the supercritical pilot plant were carried out to assess the ability of SC-CO$_2$ to extract adsorbed components. The desorption into SC-CO$_2$ was conducted under conditions of reasonable oil solubility and moderate temperature using a factorial design to determine the effects of process variables on the quantity and quality of refined orange oil.

The full factorial experiment design consisted of 18 treatment combinations (3 temperatures × 3 pressures × 2 flow rates), which were trialed in 22 runs. Four of the 18 treatment combinations were replicated to estimate the "pure error" variance. The process (primary) variables and the chosen levels are listed in Table 1. According to Draper and Smith (*19*) and the special design requirements of this experiment, the relationships between the coded and the original levels of the primary variables were defined as follows:

$$P \text{ (coded)} = \frac{\text{pressure} - 16.8966}{7.2414}$$

[16.8966 = (highest pressure + lowest pressure)/2; 7.2414 = (highest pressure − lowest pressure)/2];

$$T \text{ (coded)} = \frac{\text{temperature} - 45}{10}$$

Table 2. Definition of Variables Used in the Figures

variable	definition
A	limonene or terpene hydrocarbons
B	linalool or decanal or aldehydes or alcohols
10-fold concentrate	a concentrate that has 10 times the concentration of B/A as feed oil
% recovery of A or B (refer to Figure 1)	$100 \times$ (wt of component A or B in total eluate)/(total wt of same component loaded onto adsorbent)
loading ratio (refer to Figure 1)	wt of oil loaded onto adsorbent/wt of adsorbent
% of A or B remaining on column (refer to Figure 2)	$100 \times$ (wt of A or B remaining as adsorbate at the time of fraction collection)/(wt of A or B in initial adsorbate)
% recovery of B (refer to Figures 3 and 4)	$100 \times$ (total wt of B desorbed in 5 kg of CO_2)/(wt of B in initial adsorbate)
% recovery of B as 10-fold concentrate (refer to Figure 5)	$100 \times$ (total wt of B desorbed as 10-fold concentrate by 5 kg of SC-CO_2)/wt of B in initial adsorbate)

(45 is the value of the middle temperature; 10 is the interval of temperature variables); and

$$F \text{ (coded)} = f - 3$$

(3 is the average value of the two flow rates).

A range of response variables were chosen to accommodate the various practices in the flavor and fragrance industry and the practices and recommendations of other researchers (*2, 10*).

Data Processing and Expression. The variables used in data processing and presentation are defined in Table 2. The amount of adsorbate remaining on the column after desorption by 5 kg of CO_2 was defined as the zero point because, under all conditions studied, the extraction was almost complete at that value, which was taken as zero percent adsorbate remaining on the column. Before the zero point (<5 kg of CO_2), the remaining adsorbed amounts of terpene hydrocarbons and oxygenated components and the ratio of concentrations of groups of major oxygenated components to hydrocarbon components in the adsorbate were calculated at any stage of the extraction by working back from this defined zero point using the compositions of samples taken. The percentage recovery of components was defined as the total amount of components recovered in 5 kg of CO_2 divided by the total initial adsorbate of the same components, expressed as a percentage.

The percentage of components recoverable as 10-fold concentrates was calculated from the point on the extraction curve where the ratio of the concentration of the respective component to the concentration of terpene hydrocarbons in the remaining adsorbate was 10 times the ratio in the feed oil. The amount of the component still adsorbed at that point on the extraction curve was reported as the amount recoverable as a 10-fold concentrate. Linear or logarithmic interpolations were used, as appropriate, to estimate concentration values at exactly 5 kg of CO_2 or at intermediate points on the extraction curves.

Statistical Analysis. All statistical analyses were carried out using the Genstat 5 program, release 3.2 (Rothamsted Experimental Station). The program was used to fit full models comprising regression coefficients and first- and second-order functions of the three process variables—temperature, pressure, and flow rate—but the substitution of density or a function of density for one of the process variables was used to improve the fit of models. Models that accounted for <50% of the variance were not considered as useful approximations in this study.

RESULTS AND DISCUSSION

Assessment of Adsorbents. The major components of the batch of cv. Auroma navel orange oil used for adsorbent assessment as determined by GC-MS and GC are listed in Table 3. The major terpene hydrocarbons, D-limonene and β-myrcene, comprised 96.40% of the oil constituents. Linalool and decanal were the major alcohol and aldehydd, respectively, and six of the identified compounds were classified as oxidized limonene, which is in agreement with other reports (*1, 2*).

The results showed that decanal and linalool in the navel orange oil eluted from the aluminum oxide column much earlier when compared to the silica gel column, based on the loading

Table 3. Major Components of Cold-Pressed Navel Orange Oil and Fractions Collected from Silica Gel, As Determined in the Present Work (Variation between Duplicate Injections Was <5%)

compound	cold-pressed oil	fraction 1 (first)	fraction 12 (last)
monoterpenes	*97.52*	*99.52*	*96.90*
α-thujene	<0.01	nd[a]	nd
α-pinene	0.46	0.59	0.46
sabinene	0.46	0.31	0.10
β-pinene	0.03	0.03	0.03
β-myrcene	1.66	1.71	1.70
α-phellandrene	0.03	0.03	0.03
carene-3	0.09	0.10	0.09
α-terpenene	<0.01	nd	nd
p-cymene	<0.01	nd	nd
limonene	94.74	96.69	94.43
ocimene (*trans*)	0.03	0.03	0.03
γ-terpinene	<0.01	0.02	0.02
terpinolene	0.02	0.02	0.02
aliphatic aldehydes	*0.75*	*nd*	*0.07*
n-octanal	0.22	nd	0.02
n-nonanal	0.04	nd	0.01
decanal	0.38	nd	0.04
dodecanal	0.11	nd	nd
terpene aldehydes	*0.23*	*nd*	*0.01*
citronellal	0.05	nd	0.01
neral	0.02	nd	nd
geranial	0.03	nd	nd
perillaldehyde	0.06	nd	nd
β-sinensal	0.03	nd	nd
α-sinensal	0.04	nd	nd
alcohols	*0.58*	*nd*	*nd*
n-octanol	0.12	nd	nd
linalool	0.40	nd	nd
α-terpineol	0.06	nd	nd
oxidized limonene	*0.33*	*nd*	*0.02*
limonene oxide (*cis*)	0.08	nd	nd
limonene oxide (*trans*)	0.05	nd	nd
dehydro carveol (iso)	0.01	nd	0.02
carveol (*trans*)	0.05	nd	nd
carveol (*cis*)	0.05	nd	nd
carvone	0.08	nd	nd
esters	*0.02*	*nd*	*0.02*
neryl acetate	0.01	nd	0.02
geranyl acetate	0.01	nd	nd
sesquiterpenes	*0.13*	*0.18*	*0.12*
α-copaene	0.01	0.02	nd
β-cubebene	0.01	0.01	nd
β-caryophyllene	0.01	0.02	0.01
β-farnesene	0.02	0.02	0.02
germacrene-D	0.01	0.01	0.01
valencene	0.03	0.05	0.04
α-farnesene	0.02	0.02	0.02
δ-cadinene	0.02	0.03	0.02

[a] nd, not detected.

ratio of oil to adsorbent (Figure 1). The inset of Figure 1b is an enlargement of the graphical data of Figure 1b, clearly showing the beginning of the elution of decanal from silica gel at a

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Table 4. Major Components in Cold-Pressed Raw Valencia Orange Oil and Different Fractions[a]

	feed oil	drained fraction	depressurized fraction	desorbed fraction 1	desorbed fraction 4	desorbed fraction 7
			Weight of Fraction (Grams)			
	487.88	331.59	53.75	22.22	10.83	1.08
			Concentration (Milligrams per Gram of Fraction)			
α-pinene	3.75	2.73	2.68	2.52	2.20	1.44
sabinene	1.90	1.54	1.53	1.26	1.14	0.80
β-pinene	0.14	0.11	0.11	0.10	0.10	0.08
β-myrcene	15.65	13.13	13.01	11.97	10.73	7.44
α-phellandrene	0.20	0.16	0.16	0.16	0.15	0.14
carene-3	0.82	0.68	0.66	0.63	0.60	0.41
limonene	907.71	954.75	939.30	866.25	793.35	494.04
n-octanal	0.99	0.00	0.03	2.34	6.53	10.44
n-nonanal	0.29	0.00	0.03	0.66	0.00	0.00
decanal	2.69	0.00	0.55	6.79	19.10	53.15
citronellal	0.35	0.00	0.00	0.91	2.64	4.20
neral	0.29	0.00	0.00	1.07	2.33	3.34
geranial	0.57	0.00	0.00	2.18	5.03	7.75
perillaldehyde	0.66	0.00	0.00	3.37	6.41	15.36
n-octanol	1.39	0.00	0.00	5.29	8.72	13.71
linalool	3.72	0.04	0.00	12.58	28.39	39.66
α-terpineol	0.86	0.00	0.00	3.40	5.69	11.60
limonene oxide (cis)	0.71	0.00	0.00	1.65	4.69	9.29
limonene oxide (trans)	0.38	0.00	0.00	1.01	3.34	6.12
carveol (cis)	0.28	0.00	0.00	1.08	1.86	4.24
carveol (trans)	0.35	0.00	0.00	0.98	2.08	6.39
carvone	0.49	0.00	0.00	0.96	2.38	6.61
valencene	0.72	0.90	0.91	0.79	0.77	0.57
δ-cadinene	0.15	0.19	0.19	0.18	0.17	0.13

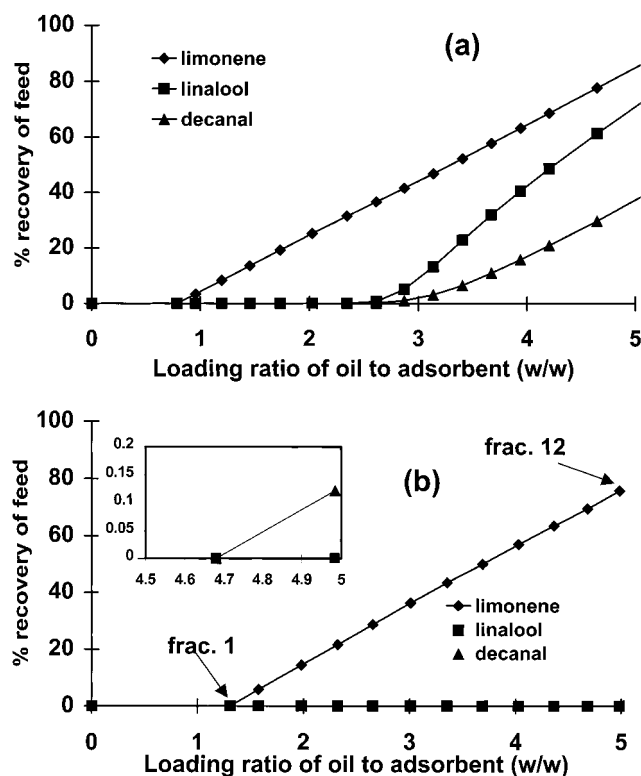[a] CO₂ conditions: 13.10 MPa × 35 °C × 2 kg/h.

Figure 1. Breakthrough of navel orange oil on aluminum oxide (a) or silica gel (b) versus loading ratio of oil to adsorbent (w/w). (Inset) Magnification of the linalool and decanal data approaching decanal breakthrough.

loading ratio of 4.7 g of navel oil/g of adsorbent. In contrast, no linalool had eluted even when the loading ratio reached 5. The compositions of the first and last eluting fractions (Figure 1b) are listed in Table 3 as fractions 1 and 12, respectively. On

the basis of the maximum adsorbent capacity for decanal, silica gel had a higher adsorption capacity for orange oil (~4.7 g of oil/g of adsorbent) than aluminum oxide (~2.7 g of oil/g of adsorbent). The adsorptive capacity of Silica Gel 60 (70−230 mesh) was slightly higher than the value of 4.4 g of oil/g of silica gel reported by Ferrer and Matthews (5).

Selective Adsorption by Silica Gel in the Pilot Plant. Concentrations of 24 major components in unprocessed Valencia orange oil and different fractions collected are listed in Table 4. The oil drained from the bottom of the column contained only terpene hydrocarbons, and the depressurized fraction comprised ~10% of the feed terpene hydrocarbons and between 0 and 4% of feed aldehydes and no alcohols. The breakthrough of decanal before linalool was also previously reported when orange oil was loaded onto silica gel using SC-CO₂ at 8.8 MPa and 40 °C (20). In the present work, the combined drained and depressurized fractions containing ~75% of the feed terpene hydrocarbons were therefore called the terpene hydrocarbon fraction. The total of the amounts of limonene, α-pinene, sabinene, β-pinene, β-myrcene, α-phellandrene, carene, valencene, and δ-cadinene was used as the total yield of terpene hydrocarbons. Because 75% of the terpene hydrocarbons had thus been separated and recovered as drained and depressurized fractions, the adsorbate was then ~4 times as concentrated as the feed oil with respect to oxygenated compounds.

SC-CO₂ Desorption Curves of Oil Components. The silica gel saturated with decanal was desorbed by SC-CO₂. The detailed weights and the concentrations of 24 compounds for all fractions and CO₂ usage in 22 runs were reported previously (21). The desorption curves for terpene hydrocarbons, aldehydes, and alcohols obtained by using SC-CO₂ at 13.1 MPa and a flow rate of 2 kg/h are shown in Figure 2a for 35 °C and in Figure 2b for 45 °C. All of the desorption curves were of similar form. The percent remaining of the total recoverable amount of the component on the column decreased progressively as more carbon dioxide was passed through. The oxygenated compounds
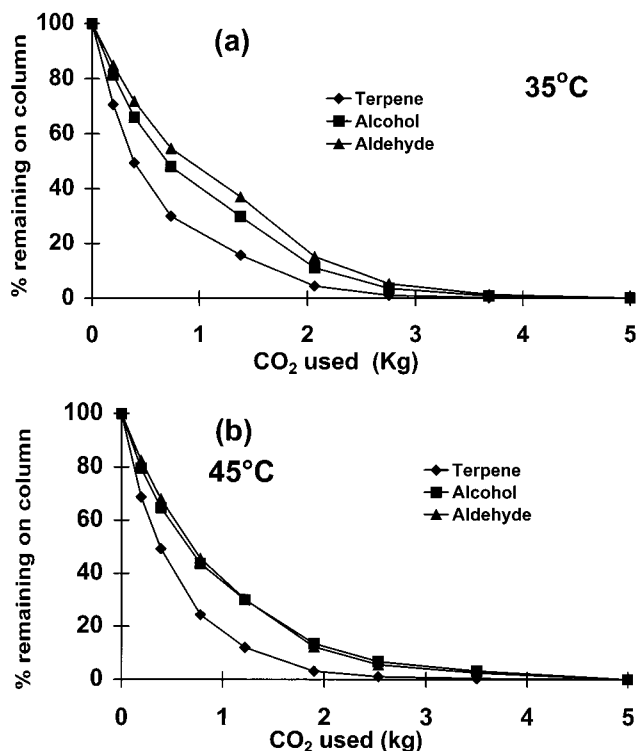
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Figure 2. Desorption curves of major classes of Valencia orange oil constituents at 13.1 MPa, 35 (a) or 45 °C (b) and 2 kg/h of CO_2.

Figure 3. Effect of SC-CO_2 density and desorption temperatures on percentage recovery of total aldehyde adsorbates using 5 kg of CO_2 at a flow rate of 2 (a) or 4 (b) kg/h.

were always desorbed later than the terpene hydrocarbons, and therefore the adsorbate remaining on the column was always richer in oxygenated compounds than the previously extracted fraction under all CO_2 conditions in this study. Its composition is the composition of the fraction yet to be collected and is referred to as the recoverable concentrate. The ratio of aldehydes and alcohols to terpenes increased as desorption progressed and the ratio depended on the temperature and pressure of the CO_2 and, to a lesser extent, the CO_2 flow rate as discussed below.

The effect of desorption temperature on the elution pattern for alcohol and aldehydes at 35 and 45 °C is shown in panels a and b of Figure 1, respectively. The separation of alcohol and aldehyde at 35 °C as opposed to an overlap at 45 °C suggested that it was possible to collect fractions of various concentrations of aldehyde and alcohol by using a lower desorption temperature of SC-CO_2.

Recovery of Total Aldehydes and Alcohols. Table 4 lists the composition of three extracts (the first, fourth, and seventh fractions) obtained by desorption with SC-CO_2 (13.1 MPa, 35 °C, and 2 kg/h). When compared with the feed oil, drained and depressurized fractions, the desorbed fractions showed increased concentrations of aldehydes and alcohols. The concentrations of decanal in the three fractions were 6.8, 19.1, and 53.2 mg/g, respectively, which were 2.5, 7.1, and 19.8 times the concentration of feed oil (2.8 mg/g). The concentrations of linalool in the three fractions were 12.6, 28.4, and 39.7 mg/g, respectively, and 3.4, 7.6, and 10.7 times the concentration of feed oil (3.7 mg/g).

The total amounts of aldehydes (*n*-octanal, *n*-nonanal, citronellal, decanal, geranial, neral, and perrillaldehyde) and alcohols (linalool, *n*-octanol, and α-terpineol) recoverable in 5 kg of CO_2 were calculated by linear interpolation of the extraction curves and expressed as percentages of the initial adsorbate of aldehydes or alcohol. The total recoveries of aldehydes and alcohols as a function of density of SC-CO_2 at
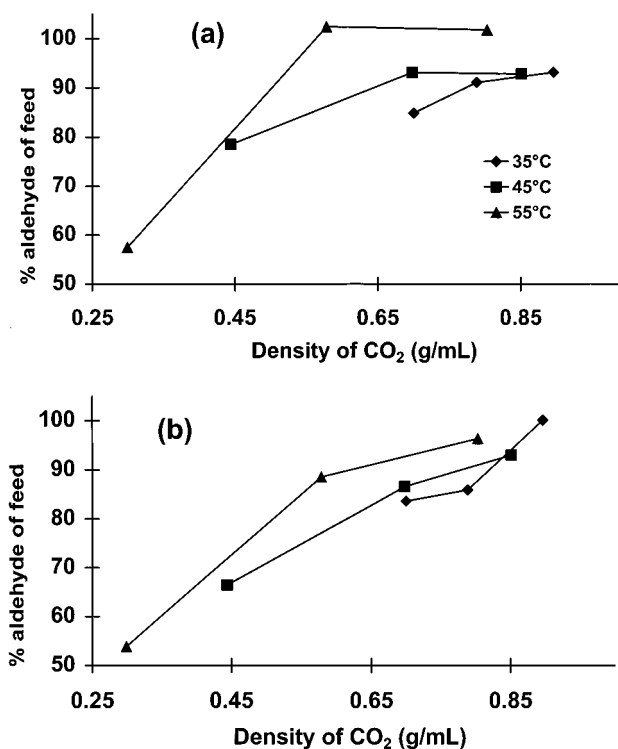
three temperatures (35, 45, and 55 °C) and two flow rates (2 and 4 kg/h) are shown in Figures 3 (aldehydes) and 4 (alcohols). The total recoveries increased at all temperatures as the density, and therefore extraction power, increased, which agreed with the results reported by Rizvi et al. (*21*). Total recoveries decreased as flow rate increased from 2 to 4 kg/h. The increased recoveries of alcohols and aldehydes at higher temperatures were due to the endothermic nature of the desorption process (*20*). The higher recovery at low flow rates suggests a closer approach to equilibrium conditions at 2 kg/h than at 4 kg/h. In a similar study, Dugo et al. (*10*) reported that SC-CO_2 desorbed 0.02 and 59.53% of oxygenated compounds in two fractions of orange oil from silica gel at densities of 0.7245 and 0.8933 g/mL, respectively, which agreed with this study.

The corresponding regression models fitted to the measured data are listed in Table 5. The model equations predict the general experimental trend in the measured data. The equations for aldehyde and alcohol estimated the values close to most of the measured data, accounting for 84.0 and 72.6%, respectively, of the observed variances. However, the measured data can be expected to approach the asymptote of 100% as density increases, whereas the simple models would not approach an asymptote above the range of densities studied. It is noteworthy that the use of CO_2 density as a process variable instead of temperature or pressure consistently improved the agreement of the results with regression models.

These models enable the effect of density on SC-CO_2 solvent properties to be viewed separately from the effect of temperature. The positive coefficient of temperature at fixed density indicated that at higher temperatures, higher total recoveries of aldehydes and alcohols were obtained, which implies that the desorption process for those compounds is endothermic. Sato et al. (*20*) reported adsorption equilibrium constants for linalool and limonene as a function of CO_2 density at 40, 50, and 60 °C, showing that adsorption equilibrium constants decreased

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Table 5. Regression Model Equations Corresponding to the Maximum Achievable R^2 for the Experimental Data[a]

response variable (Y)	equation	R^2 (%)
% recovery of total aldehyde using 5 kg of CO$_2$	$Y = -6.00 + 5.12T - 2.40F + 236.5D - 137.8D^2$	84.0
% recovery of total alcohol using 5 kg of CO$_2$	$Y = 32.9 + 3.80T + 124.9D - 0.322F + 3.47T^2 - 68.3D^2 - 2.13TF$	72.6
% recovery of aldehyde as 10-fold concentrate (aldehydes/terpenes)	$Y = 54.19 - 14.99T - 2.56P + 0.85F - 19.17P^2 - 6.77TP + 4.32PF$	61.5
% recovery of alcohol as 10-fold concentrate (alcohols/terpenes)	$Y = 20.59 - 7.49T - 10.65P - 7.24F + 3.48TP$	73.0

[a] T, P, and F are the coded temperature, pressure, and flow rate, respectively, D is the density in g/mL, and R^2 is the analysis variance.
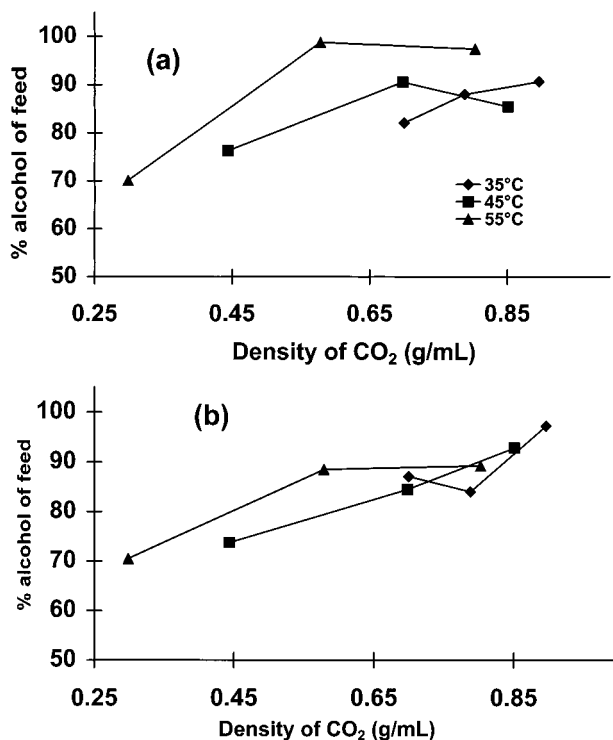
Figure 4. Effect of SC-CO$_2$ density and desorption temperatures on percentage recovery of total alcohol adsorbates using 5 kg of CO$_2$ at a flow rate of 2 (a) or 4 (b) kg/h.

Figure 5. Effect of desorption pressure and temperature on percentage recovery of aldehydes (a) or alcohols (b) equivalent to 10-fold concentrate at a SC-CO$_2$ flow rate of 2 kg/h.

with increasing temperature, thus supporting the view that the desorption process was endothermic.

From the negative coefficient of flow rate for total recovery of aldehydes in this model it appeared that the higher the flow rate, the lower the recoverable adsorbate. It is presumed that the effect of CO$_2$ flow rate on aldehyde yield was caused by greater departure from equilibrium conditions in the separation cell with increased CO$_2$ flow rate. The dependence of alcohol yield on flow rate is not consistent at different temperatures (for the measured data), although the model has a small negative coefficient for flow rate. The mass transfer property of the aldehydes is unlikely to differ greatly from those of alcohols because they have a similar range of molecular weights. However, liquid alcohols are less volatile than comparable aldehydes, and therefore it is more likely that the alcohols suffered less loss during collection with the higher flow rate of CO$_2$.

Production of 10-fold Aldehyde and Alcohol Concentrate. The 10-fold concentrate is defined as a concentrate with a ratio of aldehyde or alcohol/terpene hydrocarbons 10 times that of feed oil. The percent recoveries of aldehydes or alcohols as a 10-fold concentrate are plotted as a function of desorption pressure and temperatures at an SC-CO$_2$ flow rate of 2 kg/h in Figures 5. The total percentage recovery of aldehyde and alcohol as a 10-fold concentrate of feed initially increased to a maximum at the intermediate pressure of 13.1 MPa (apart from at 35 °C)
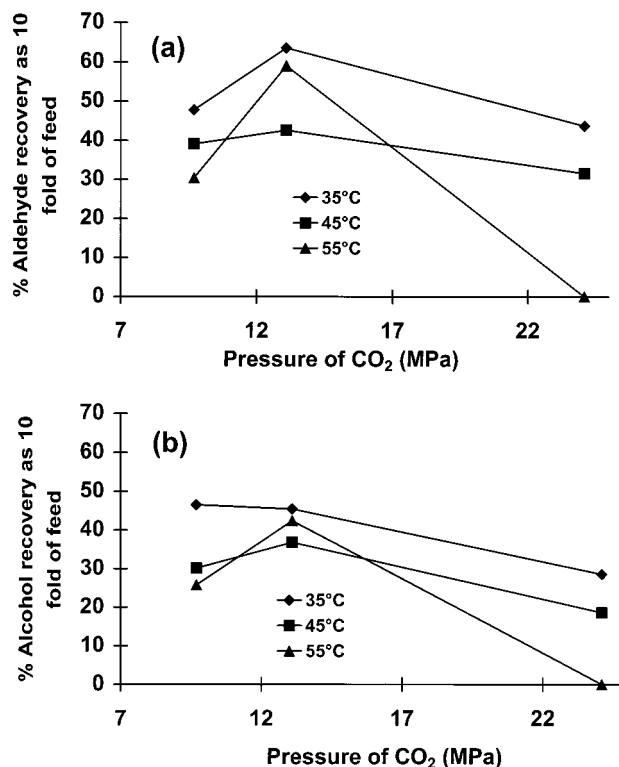
and then decreased as pressure increased further. Decrease in the recoveries at high pressures has been attributed to poor selectivity achievable at high pressures and therefore higher density (*2, 7, 10, 12, 14, 19, 20, 22−24*). The maximum recoveries of alcohol and aldehyde as 10-fold concentrates lie close to desorption conditions of 35 °C and 13.1 MPa.

The regression equations obtained by fitting the observed data are listed in Table 5. The model equations also include flow rate effects. In contrast to total recovery of aldehydes and alcohols, no simple function including density as a variable could account for >40% of the variance. The ability of fitted models to account for the variance of the measured data was not as good for the recovery of concentrates as it was for total yields. However, some trends are still seen from the fitted models, for example, that the lower the temperature, the better the separation that could be achieved. This indicates that lower temperatures improved the separation of the components of orange oil and can be explained by the effect of temperature on the equilibrium. If the adsorption of oxygenated compounds is more exothermic than the binding of terpene hydrocarbons (or the desorption of oxygenated compounds is more endothermic), retention of oxygenated compounds is favored by lower temperatures. The small and negative effect of flow rate on selectivity, as depicted by the model, is not surprising, as higher

flow rates can reduce the chromatographic effect in adsorption/desorption systems by increasing the deviation from equilibrium.

Concentration Process. It has been shown that it is feasible to concentrate orange oil flavor compounds by a process of selective removal of terpene hydrocarbons by adsorption of oxygenated compounds onto a silica gel bed followed by desorption using SC-CO_2. The process can be outlined as follows. Orange oil is loaded onto silica gel until a saturation capacity of 4.7 g of oil/g of adsorbent is reached, thus removing ∼75% of the feed terpene hydrocarbons in the first step. In the second step, desorption from the saturated adsorbent bed using SC-CO_2 at 13.1 MPa, 35 °C, and 2 kg/h is used to achieve maximum recovery of flavor compounds. More work is needed to optimize the precise process conditions of desorption to achieve specific concentration ratios of aldehydes and alcohols. Work is currently in progress in the authors' laboratory to scale-up the process.

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