Current Investigations on Orange Peel Oil Fractionation[a]

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Over the last few years, the fractionation of orange peel oil through the use of supercritical fluid carbon dioxide ($SCFCO_2$) has been a matter of intense research. Despite this fact, the deterpenation of such material has still been conducted in several industries by means of vacuum distillation. In this work we present results using an automatic vacuum distillation column operated in the semi-batch mode over the temperature range of 50°-80°C, from 10 to 30 mbar and with a reflux ratio of 0.25 and 0.75. As in the case of vacuum distillation, an experimental design was adopted to perform the extractions using $SCCO_2$ in a high-pressure column operated in the countercurrent mode in the range of 50°-70°C, from 70-100 atm and with a solvent to oil mass ratio up to 60. Phase equilibrium data for the system CO_2-orange peel oil, which are essential for the high-pressure fractionation, are provided in a wide range of temperature and pressure. The results of orange peel oil fractionation are presented and analyzed with regard to the content of oxygenated compounds and sensory analysis.

Introduction

Citrus oil is a mixture of high volatile components such as mono- and sesquiterpene hydrocarbons, oxygenated compounds and non-volatiles such as pigments and waxes. In spite of the high content, the monoterpene hydrocarbons, they do not contribute much to the flavor or fragrance of the oil. Because they are unstable to heat and light, monoterpene hydrocarbons must be removed to stabilize the oil. The odoriferous of a citrus oil consists of alcohols, aldehydes and ketones that provide much of its characteristic flavor.

In the past few years, citrus oil fractionation has received an increased attention due to the direct application of folded and terpeneless oils in the food and pharmaceutical industries. The fractionation of these oils has been commonly performed using conventional techniques, such as vacuum distillation. Unfortunately little information on this subject is available in the open literature.[1]

Recently, the efforts in this area of citrus oil fractionation have been directed toward the use of supercritical fluid CO_2 ($SEFCO_2$) using a variety of equipment operating in different modes, since the separation can be performed at low temperatures. A review of the literature shows that $SCFCO_2$ extraction of citrus oils yields a terpene fraction (distillate), which is almost free of oxygenated components, and a concentrate, which is rich in oxygenated odoriferous components.[2-5]

A variety of $SCFCO_2$ extraction simulations have been conducted in an attempt to establish the best operating conditions and to provide a first approach to the scale-up of such processes.[6,7] Nevertheless, this step has been generally accomplished using thermodynamic properties and phase equilibrium data only involving the most representative compounds present in the citrus oil, i.e., limonene and linalool, in the case of orange peel oil, which means an oversimplified modeling technique. Of course, progress in this field has been hindered by the lack of a more comprehensive work concerning the phase equilibrium behavior of CO_2-orange peel oil.[8]

In this sense, high-pressure vapor-liquid equilibrium data for this system is provided affording the construction of the PT-xy diagram using the temperature and pressure ranges of practical interest. The experimental technique used here to investigate the phase equilibrium can be classified as theoretical or an indirect method in which the equilibrium composition might be determined without sampling. The advantage of an equilibrium cell with visual capabilities is that the phase separation can be observed directly thus eliminating the possibility of missing an additional equilibrium phase. Excellent reviews about experimental techniques of high-pressure phase equilibrium can be found in the work of Fornari et al.[9] and Dohrn and Brunner.[10]

The main objective of this work is to present our experimental findings concerning the deterpenation of orange peel oil using a vacuum distillation column and some insights into the use of $SCFCO_2$ in a packed high-pressure extraction column. Also, phase equilibrium data for the CO_2-orange peel oil system over a wide range of temperature and pressure are reported.

Experimental

Cold-pressed orange peel oil (Citrus sinensis Osbeck) was kindly supplied by Citrosuco S.A. and used with further treatment. Carbon dioxide, with a grade better than 99.9 percent, was purchased from AGA S.A. Experimental results obtained were evaluated by GC/MS and by sensory analysis performed by Citrosuco S.A. and EMBRAPA/Food Technology.

GC/MS: Gas chromatography/mass spectroscopic analyses were performed by injecting 0.04 μL samples, with a 100:1 split, into a Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionization detector and connected to a mass spectrometer Hewlett-Packard 5970. A fused silica capillary column, 25 m x 0.2 mm cross-linked with polyethylene glycol-TPA modified (FFAP) was used. Column temperature was programmed from 60°-200°C at 5°C/min. Hydrogen flow rate was 1 mL/min. Injection port temperature was 250°C and detector temperature 280°C. Percentages were calculated by the internal normalization method.

Vacuum distillation: An automatic vacuum distillation column (1.30 m height, 15 mm i.d.) packed with Raschig rings (Karl Kolb Scientific Supplier, Vakuumat-X) was employed in the oil fractionation tests. Typically, about 200 mL of orange peel oil was fed into the column bottom (pot) and the temperature and pressure were adjusted to the desired values and the operation started after 1 h of total reflux in order to allow equilibrium to be achieved. Afterwards, a pre-established reflux ratio was set and samples were collected from the top (distillate) and bottom (concentrate) until approximately 5-fold concentrate, based on the bass of the original raw oil, was reached. Five-fold oil is one which is concentrated 1/5 of its original weight. Duplicate runs were accomplished leading to a reproducibility better than 0.4 fold.

Vapor-liquid equilibrium: The phase equilibrium experiments (cloud points) were performed in a high-pressure variable-volume view cell. The apparatus consists basically of a view-cell, having three sapphire windows, an absolute pressure transducer (Smar LD 301), with a precision of ±0.012 Mpa, a portable programmer (Smar, HT 201), for the pressure data acquisition, and a syringe pump (ISCO 260D). The equilibrium cell has an internal volume of 28 mL and contains a movable piston, which permits the pressure control inside the cell. Phase transitions were recorded visually as bubble or dew points just varying the pressure in the back of the piston. The cell was equipped with an electrical heater and a temperature controller (Dextron, DTS4) connected to a thermocouple placed into the cell. This arrangement provided a temperature control with a precision of 0.5°C.

| Table 1. Experimental planning and results for the vacuum distillation of orange peel oil						
Run	P (mbar)	RR	Oxygenates %	Fold (g/g)	CF	Sensory analysis
1	30	0.75	6.17	4.3	4.6	worst
2	30	0.50	6.73	4.5	4.7	worst
3	30	0.25	6.57	4.4	4.7	worst
4	20	0.75	8.58	5.5	6.2	best
5	20	0.50	7.55	5.1	5.5	worst
6	20	0.25	8.14	5.3	5.9	intermediate
7	10	0.75	7.42	4.9	5.6	intermediate
8	10	0.50	8.14	5.3	6.3	best
9	10	0.25	8.41	5.5	6.0	intermediate

RR = reflux ratio; Oxygenates % = alcohols, aldehydes, esters, ketones and acids; CF = concentration factor

Figure 1. PT-xy diagram for the system CO_2-orange peel oil

Amounts of orange peel oil (measured gravimetrically) and CO_2 (measured by the volume changes of the syringe pump reservoir) were charged into the cell to results in a pre-established global composition. Then, the mixture was continuously agitated by means of a magnetic stirrer and the pressure was increased, at constant temperature, until the observation of the presence of one phase and decreased to the incipient formation of a two-phase system. The equilibrium pressure was then recorded after repeating this procedure at least five times, leading to a reproducibility better than 0.68 atm.

Supercritical extraction: The fractionation was also carried out in a high-pressure extraction column (1 m height, 38 mm i.d.) structured with Sulzer CY (Sitec-Engineering) in the countercurrent continuous mode. The column was operated in trickle flow (continuous $SCFCO_2$ phase) and after reaching the desired temperature and pressure, CO_2 and oil were continuously fed by means of two high pressure pumps (TSP 3200 P/F) at a pre-established CO_2/oil mass ratio (S/F). The operating time was fixed in 6 hours based on the residence time of incoming fluids. The pressure was monitored using an absolute pressure transducer (Smar LD 301) and the concentrate flow was controlled by the column level control. Duplicate runs were accomplished giving a reproducibility better than 0.1 fold.

Results and Discussion

Vacuum distillation: First, it has been adopted an experimental planning in order to maximize the aldehyde content in the concentrated oil in the temperature range of 50°-80°C, from 10 to 30 mbar and a reflux ratio (RR) of 0.25 to 0.75. From these preliminary runs it was found that only at 80°C was it possible to concentrate the raw oil in acceptable levels. Then, a new experimental design was conceived keeping the temperature constant and varying the pressure and the reflux ratio as presented in Table 1. The concentration factor (CF) has been defined as the relative percent of oxygenates
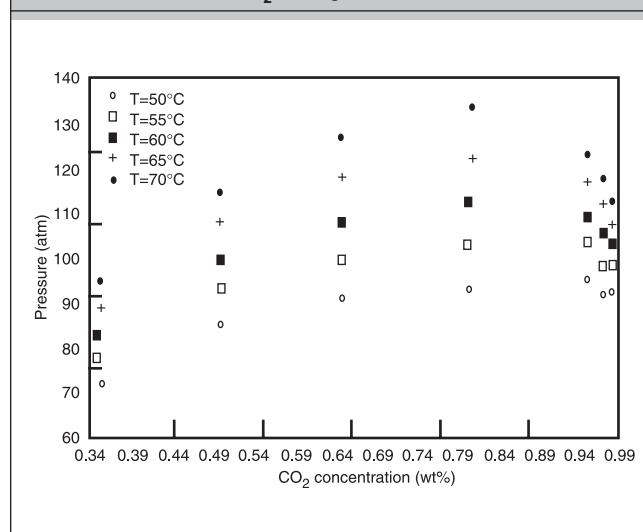
(linalool + decanal) in the concentrated oil and in the raw oil (linalool + decanal % = 0.66) and the oxygenates % as being relative to alcohols, aldehydes, esters, ketones and acids.

One can observe from Table 1 that all samples obtained at 30 mbar were considered to have the poorest odor quality as judged by sensory analysis. These samples also showed the lowest concentration factors. At this pressure, the extraction process of terpenic hydrocarbons was not selective probably due to the proximity of the vapor pressure curve of limonene thus making difficult its separation from the concentrate. It should be noted; however, that at 20 mbar, samples were considered as having the best, worst and intermediate odor qualities by just varying the reflux ratio. In general, samples produced at 10 mbar were considered to possess the most desired aroma characteristics. The main constituents present in orange oil concentrate were identified and are listed in Table 2.

It can be observed from this table that the runs 4 (20 mbar; R = 0.75) and 8 (10 mbar, RR = 0.50) led to the best performance according to sensory analysis and they provided the highest linalool and decanal content in the concentrate, as expressed by the concentration factor. Note that the concentration factor values corroborated the results of the sensory analysis. It seems that there was a maximum in the oil quality as a function of pressure and reflux ratio. Though some experiments result in an oxygenated-compounds percent close to the assigned concentrate with the most desired odor, it is accepted that the sensory analysis together with the concentration factor should be the final answer to this question.

Vapor-Liquid Equilibrium: Phase equilibrium data for CO_2-orange peel oil were measured at the temperatures of 50, 55, 60, 65 and 70°C and at global CO_2 compositions (wt %) of 0.35, 0.50, 0.65, 0.80, 0.95, 0.97 and 0.98. The transition types observed at each temperature were recognized as either by a bubble point (BP) or a dew point (DP). In the experiments, DP transitions were characterized by the

Table 2. Quantitative composition (%) of concentrated orange peel oil by vacuum distillation								
				Run				
Compound	1	2	3	4	5	6	7	8	9
myrcene	0.14	0.10	0.13	0.15	0.13	0.13	0.09	0.11	0.12
limonene	92.09	91.43	91.61	89.10	90.15	89.59	90.60	89.70	89.31
octanal	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
citronellal	0.25	0.26	0.26	0.34	0.30	0.32	0.29	0.31	0.33
decanal	1.31	1.41	1.37	1.81	1.59	1.69	1.53	1.69	1.77
linalool	1.91	2.10	2.03	2.71	2.27	2.42	2.32	2.62	2.57
neral	0.18	0.19	0.18	0.24	0.21	0.23	0.20	0.22	0.23
geranial	0.41	0.44	0.43	0.57	0.49	0.53	0.47	0.53	0.55

Table 3. Experimental planning and results for the supercritical CO_2 fractionation of orange peel oil

Run	P (°C)	P (atm)	Oxygenates S/F	Fold %	(g/g)	Sensory CF	analysis
1	50	70	40	1.90	1.2	1.04	worst
2	50	80	40	1.92	1.2	1.04	worst
3	50	70	60	2.00	1.0	1.09	intermediate
4	50	80	60	2.01	1.1	1.09	intermediate
5	60	80	40	2.00	1.1	1.05	worst
6	60	90	40	2.12	1.2	1.14	intermediate
7	60	80	60	2.26	1.2	1.15	intermediate
8	60	90	60	2.41	1.4	1.23	reasonable
9	70	90	40	2.03	1.2	1.09	intermediate
10	70	100	40	2.14	1.2	1.10	intermediate
11	70	90	60	2.20	1.2	1.17	intermediate
12	70	100	60	2.31	1.3	1.24	reasonable
13	60	85	50	2.15	1.2	1.12	intermediate

S/F = solvent/oil mass ratio; Oxygenates % = alcohols, aldehydes, esters, ketones and acids; CF = concentration factor

formation of drops of the heavier phase at the bottom of the cell preceded by a complete opalescence of the solution. In BP transitions, small bubbles arise from the middle of the cell with a subsequent formation of a lighter phase at the top of the cell.

In Figure 1 the PT-xy diagram for CO_2-orange peel oil is presented. The experimental data are in good qualitative agreement with those published in the literature.[4] It is interesting to note in this Figure, that at lower temperatures slight changes in pressure led to large variations of the liquid phase compositions. As the temperature was raised the plateau became less pronounced. This might be a very important point since more stable operating regions may be reached at higher temperatures if one realized a $SCFCO_2$ fractionation step. Of course, energy costs should also be taken into account in spite of the process separation efficiency.

Supercritical Extraction: Based on the phase equilibrium data obtained in this work, an experimental design

Figure 2. Effect of solvent density on the concentration factor at different solvent/oil mass ratio
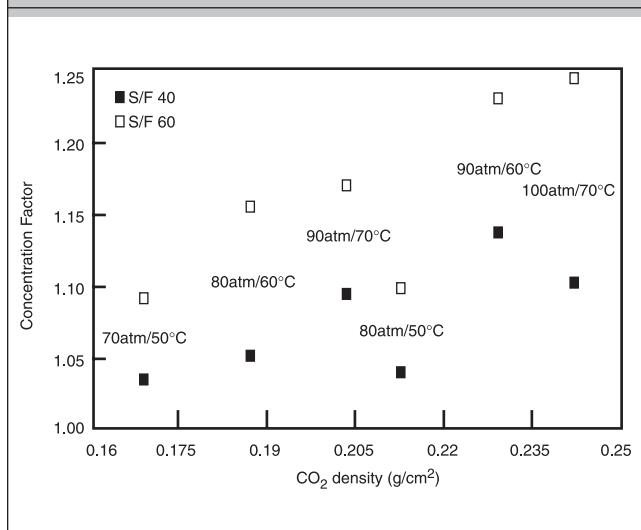
was adopted to perform the fractionation using $SCFCO_2$ in a high-pressure column in the range of 50°-70°C, from 70-100 atm and with a solvent to oil mass ratio up to 60. These operating conditions not only take the phase equilibrium data into account but also consider our recent simulation results[7] and the costs related to solvent feed involved in

such process.[4] The results obtained from the experimental design are presented in Table 3.

Although the results obtained from $SCFCO_2$ fractionation may not be considered satisfactory from a commercial point of view, it can be concluded that the operating conditions affect the characteristics of the concentrated oil. Figure 2 shows the effect of solvent density on the concentration factor of oxygenated components in the concentrate. From this figure and Table 3 one can see that the concentration factor increased with increasing S/F (CO_2/oil mass ratio), over the temperature and pressure ranges investigated. At S/F of 40the results were inferior to those obtained at S/F of 60 for all conditions. At constant temperature, a raise in CO_2 density led to an enhancement of the concentration factor due to an increase of the so-called solvent power. The main compounds as analyzed by GC/MS are presented in Table 4.

It is noteworthy from Figure 2 and Table 3 that samples eight (60°C, 90 atm, S/F = 60) and 12 (70°C, 100 atm, S/F = 60), considered reasonable by the sensory analysis, were obtained at the conditions with the greatest concentration factors; the other samples were considered inferior.

A relevant information obtained from the experiments performed was that the best operating temperature was situated in the interval of 60°-70°C, avoiding the degradation

of thermolabile compounds. At 50°C, the results were not satisfactory for all experimental conditions. Büdich et al.[4] have determined 60°C as being the best temperature for the fractionation process due to the highest solubility values achieved, besides being favorable regarding the economic costs and low product degradation.

The main limitation of the experimental setup used by us was certainly the low flow rate provided by the high-pressure liquid pumps resulting in a poor contact between the continuous and disperse phases thus limiting the mass transfer process. Another important aspect that needs to be taken into account was the wax retention. Not only waxes may reduce the efficiency of the packing in the extraction column for long operation times but also they may cause the appearance of preferential paths along the extraction column.[3]

Further research in this field is necessary to improve the efficiency of the countercurrent process. Since the objective is to produce flavor fractions of a high market value, supercritical countercurrent deterpenation is believed to be competitive to conventional processes.

Acknowledgments

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Table 4. Quantitative composition (%) of concentrated orange peel oil by SCFCO₂

| | Run | | | |
Compound	1	2	3	4
myrcene	1.64	1.66	1.61	1.59
limonene	95.32	95.14	95.08	94.43
octanal	0.16	0.16	0.16	0.17
citronellal	0.09	0.05	0.06	0.03
decanal	0.23	0.23	0.23	0.25
linalool	0.46	0.47	0.49	0.48
neral	0.03	0.03	0.03	0.04
geranial	0.18	0.20	0.23	0.35

| | Run | | | | |
Compound	5	6	7	8	13
myrcene	1.54	1.52	1.48	1.39	1.48
limonene	94.82	94.55	93.95	94.01	94.33
octanal	0.16	0.16	0.16	0.15	0.16
citronellal	0.03	0.07	0.03	0.03	0.03
decanal	0.22	0.25	0.23	0.26	0.23
linalool	0.48	0.51	0.54	0.56	0.51
neral	0.03	0.03	0.03	0.03	0.03
geranial	0.25	0.28	0.43	0.34	0.35

| | Run | | | |
	9	10	11	12
myrcene	1.57	1.54	1.40	1.42
limonene	94.67	94.98	94.33	93.84
octanal	0.16	0.16	0.15	0.16
citronellal	0.06	0.04	0.03	0.04
decanal	0.23	0.24	0.24	0.27
linalool	0.50	0.49	0.54	0.56
neral	0.03	0.03	0.03	0.04
geranial	0.31	0.24	0.36	0.40