Deterpenation of Brazilian Orange Peel Oil by Vacuum Distillation

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ABSTRACT: The deterpenation of orange peel oil in most industries is accomplished by vacuum distillation, but surprisingly little information on this matter can be found in the open literature. This work reports recent results on orange peel oil deterpenation carried out in an automatic vacuum distillation column operated in the semibatch mode at the temperatures of 50, 65, and 80°C, at 10, 20, and 30 mbar, and with reflux ratios of 0.25, 0.50, and 0.75. The concentrates were analyzed with regard to the oxygenate compound content by gas chromatography coupled with a mass spectrometer (GC–MS) and evaluated by sensory analysis, and also with regard to the aldehyde content. As one could expect, there is a strong relationship between oil quality, as revealed by the sensory analysis, and chemical composition, as determined by GC–MS. The concentration factor and process yield, as expressed by "fold," together with the analysis results show that it is possible to obtain high quality concentrates simply by manipulating the operating variables in the vacuum fractionation process.

Paper no. J9946 in *JAOCS 78,* 1041–1044 (October 2001).

KEY WORDS: Chemical composition, concentrate, flavors, fractionation, orange peel oil, vacuum distillation.

Citrus peel oils are important flavoring ingredients for flavor, beverage, food, cosmetic, pharmaceutical, and chemical products. Cold-pressed oil, also called citrus peel oil, is a mixture of highly volatile components such as terpene and oxygenated hydrocarbons and nonvolatiles such as pigments and waxes. Despite the high content, the terpene hydrocarbons do not contribute much to the flavor or fragrance of the oil, and because they are unstable to heat and light, they must be removed to stabilize the final product. The oxygenated compound fraction provides much of the characteristic flavor strength of citrus oils and consists mainly of alcohols, aldehydes, and ketones.

Over the past few years, the possibility of fractionating citrus oils has received increased attention because of the direct industrial applications of the high value-added products generated. The factors of economics, required flavor concentration, and degree of stability generally determine the extent of "folding" by the trade. One of the most widely used concentrated citrus oils is a fivefold concentrate from the original oil.

Though new fractionation techniques such as the use of compressed gases have been reported in the literature, the deterpenation of citrus oils has still been conducted in several industries by means of vacuum distillation (1–3). Perhaps the best example on this subject is orange peel oil processing in Brazil, recognized as being one of the world's leading orange juice producers. Owing primarily to fluctuations in orange production and to different and constantly changing demands from importing countries, the industrial research efforts have been headed for improving process efficiency as well as achieving quality specifications. However, a little information about the deterpenation of orange peel oil is available in the open literature.

Lifshitz *et al.* (4) reported that upon 10-fold concentration of orange peel oil, parameters such as specific gravity and aldehyde content changed linearly with concentration. Nevertheless, they did not report any quantitative values for individual compounds. Vora *et al.* (5) concentrated Valencia and Midseason orange peel oil by vacuum distillation to 10- and 25-fold at 57–62°C and 10 mm Hg. Flavor and color concentrates were analyzed by gas chromatography and identified by mass spectrometry (GC–MS). Their results showed that very different compositions may be obtained from different raw materials, thus influencing the color and flavor characteristics of the oil.

In this context, this work is aimed at presenting our findings concerning the deterpenation of Brazilian orange peel oil using a vacuum distillation column operated in the semibatch mode at the temperatures of 50, 65, and 80°C, at 10, 20, and 30 mbar, and with reflux ratios (RR) of 0.25, 0.50, and 0.75. For this purpose, a two-level, three-variable (temperature, pressure, and RR) experimental design was adopted so as to assess the influence of the process variables on the qualitative sensory analysis (standardized test) and chemical composition of the prepared concentrates (6).

EXPERIMENTAL PROCEDURES

Brazilian orange peel oil (*Citrus sinensis Osbeck*) was kindly supplied by Citrosuco S.A. (Matão, São Paulo, Brazil). The oil was obtained by FMC (Lakeland, FL) in-line juice extractors during orange juice extraction. A crude oil emulsion was obtained from the juice extractor, centrifuged in order to separate the oil from the water, and winterized to remove paraffin waxes. Experimental results were evaluated by total aldehyde content, GC–MS and by sensory analysis performed by Citrosuco S.A. and Embrapa/Food Technology.

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An automatic vacuum distillation column (1.30 m ht, 15 mm i.d.), operated in the semibatch mode, packed with Raschig rings (Vakuumat-X; Karl Kolb Scientific Supplier, Wertheim, Germany) was employed in the oil fractionation experiments. Typically, about 200 mL of orange peel oil was fed into the column bottom, the temperature and pressure were adjusted to the desired values, and the operation was started after 1 h of total reflux so as to allow the stabilization of all components of the equipment. Then, a pre-established RR was set, and samples were collected from the top (distillate) and bottom (concentrate) after 3 h of operation time (first experimental design). Taking into account commercial aspects, the researchers carried out a second experimental design toward obtaining a fivefold concentrate (based on the mass of the original raw oil). Duplicate runs were accomplished for all experimental conditions leading to a maximal average deviation of 0.33-fold. Here, it might be important to call attention to the fact that the first experimental design involved a constant operation time (3 h), whereas the experiments in the second experimental design were conducted until approximately 20% wt of the original oil (a fivefold oil) remained inside the distillation flask. For instance, at 80°C and 10 mbar the experiments lasted about 90 min.

GC–MS. GC analyses were performed by injecting 1.0 µL samples, with a 150:1 split, into a Hewlett-Packard 5890A gas chromatograph (Avondale, PA) equipped with a flame ionization detector and connected to a Hewlett-Packard 5970 mass spectrometer (Palo Alto, CA). A fused-silica capillary column, (30 m × 0.25 mm i.d., 0.25 µm film thickness) coated with a DB5 (J&W Scientific, Folsom, CA) stationary phase was used. Column temperature was programmed from 40–180°C at 5°C/min. Hydrogen flow rate was 1 mL/min through the column. Injection port temperature was 250°C and detector temperature 280°C. Chemical constituents of orange oil samples were identified by MS with similar GC conditions as described above. The sample components were identified by matching their mass spectra with those from the WILEY database library. Percentages were calculated by the internal normalization method.

Aldehyde content and sensory analyses. Total aldehyde content of orange oil samples, as a percentage of decanal, were determined following the procedure described in the *United States Pharmacopeia* (7). The sensory analyses were performed by the Citrosuco S.A. industry by means of at least four professional tasters. According to Citrosuco S.A., samples were compared to each other and to a standard industrial sample. They were then classified as worst (6.0–6.5), intermediate (6.5–7.0), and best (7.0–7.5), the latter being very close to the quality requirements of the mentioned industry.

RESULTS AND DISCUSSION

Initially, a two-level experimental design, with three variables, at the temperatures of 50–80°C, from 10 to 30 mbar, and with RR of 0.25–0.75 (Table 1), was adopted. The concentration factor (CF) was defined as the percentage of oxygenates (linalool + decanal) in the concentrated oil compared to that in the raw oil (linalool + decanal % = 0.57). Samples obtained from both experimental designs were evaluated by chemical (aldehyde content) and chromatographic analyses; sensory analysis was performed for the second experimental design only.

TABLE 1
Results for the Vacuum Distillation of Orange Peel Oil for the First Experimental Design (constant operation time, 3 h)[a]

Run	T (°C)	P (mbar)	RR	Oxygenates (%)	Fold (g/g)	CF	Aldehyde total (%)
1	50	10	0.25	0.62	1.05	1.09	1.68
2	50	10	0.75	0.61	1.04	1.07	1.56
3	50	30	0.25	0.64	1.01	1.12	1.47
4	50	30	0.75	0.61	1.01	1.07	1.32
5	80	10	0.25	30.32	25.00	53.19	9.60
6	80	10	0.75	15.42	13.30	27.05	7.12
7	80	30	0.25	4.90	7.14	8.59	3.64
8	80	30	0.75	2.11	3.45	3.70	2.32
9	65	20	0.50	0.60	1.02	1.05	1.57

[a] T, temperature; P, pressure; RR, reflux ratio; oxygenates (%), linalool + decanal; CF, concentration factor.

According to the Brazilian citrus industries, the total aldehyde content (as decanal) should be in the range of 3–3.8% and 6–6.8% for 5- and 8.5-fold oil, respectively, whereas the raw oil presents around 1.2%. It can be observed from Table 1 that the aldehyde content in run 7 (3.64% and 7.14-fold) corresponds to an expected value for fivefold oil. Most probably, decanal has been carried in the terpene hydrocarbon stream during the concentration process.

It is worth noticing from this table that it was not possible to concentrate the oil at 50°C regardless of the operating pressure. This result was expected because at this temperature the vapor pressure of limonene and linalool are quite similar, thus making the separation a difficult task. Moreover, 65°C did not lead to good results due to head losses coming from the column geometry (small inner diameter compared to the column height).

At 80°C, on the other hand, the results were very sensitive to variations in the operating variables. For instance, a decrease in pressure at constant RR led to a remarkable increase in all figures, whereas a raise in RR at constant pressure caused a reduction of all the output variables. The main constituents present in the concentrated orange oil, for the first design, were identified and are listed in Table 2.

From these preliminary results it became clear that only at 80°C was it possible to concentrate the raw oil with the present apparatus to acceptable levels. In an attempt to better explore the vacuum fractionation process, a new experimental design was conceived, keeping the temperature constant (80°C) and varying the pressure, RR and, of course, the operation time, as presented in Table 3. Note that at this step the aldehyde content in the concentrated oil achieved a value as high as or even higher than the corresponding level of 8.5-fold oil.

One can observe from Table 3 that all samples obtained at 30 mbar were considered the worst by the sensory analysis, also showing the lowest CF. At this pressure value, the extraction process of terpenic hydrocarbons was not selective, probably due to the proximity to the vapor pressure curve of

TABLE 2
Quantitative Composition (%) of Concentrated Orange Oil by Vacuum Distillation for the First Experimental Design (constant operation time, 3 h)[a]

	Experiment								
Compound	1	2	3	4	5	6	7	8	9
α-Pinene	0.37	0.37	0.43	0.43	—[b]	—	-	-	0.33
β-Pinene	0.02	—	—	0.02	—	—	—	—	—
Sabinene	0.23	0.22	0.24	0.24	—	—	—	—	0.21
Myrcene	1.53	1.61	1.66	1.60	—	0.09	0.04	0.13	1.55
Limonene	95.17	95.82	95.85	95.36	1.40	56.01	85.95	93.51	95.65
Phellandrene	0.21	0.23	0.21	0.25	—	0.07	0.16	0.18	0.22
γ-Terpinene	0.03	0.05	—	0.03	—	0.17	0.06	0.05	0.04
ρ-Cimene	0.02	—	—	0.02	—	—	—	—	0.06
Octanal	0.19	0.19	0.25	0.18	—	0.43	0.15	0.07	0.18
Nonanal	0.04	—	—	0.04	1.21	0.98	0.35	0.07	0.01
Citronellal	0.03	—	—	0.02	2.18	0.74	0.26	0.11	0.01
Decanal	0.18	0.17	0.20	0.18	9.44	3.82	1.52	0.59	0.17
Linalool	0.44	0.44	0.44	0.43	20.88	11.60	3.38	1.52	0.43
Octanol	0.03	—	—	0.01	0.77	0.74	0.15	0.09	—
Neral	0.03	—	—	0.03	2.22	0.80	0.26	0.12	0.12
α-Terpineol	0.09	0.09	0.09	0.08	4.32	1.53	0.54	0.26	0.08
Geranial	0.22	0.19	0.19	0.18	9.99	2.97	1.05	0.53	0.20

[a] See Table 1 for experimental parameters.
[b] —, traces.

limonene. It should be noticed, however, that at 20 mbar, samples were considered as best, worst, and intermediate just by varying the RR. In general, samples produced at 10 mbar were considered the best ones. The main constituents present in the concentrated orange oil for the second design are presented in Table 4. A decrease in limonene concentration and an increase in concentration of linalool and decanal in orange concentrate is illustrated in Figure 1.

It can be observed from this table that runs 4 (20 mbar; RR = 0.75) and 8 (10 mbar; RR = 0.50) led to the best performance according to the sensory analysis, and they provided the highest linalool and decanal content in the concentrate, as expressed by the CF. Note that the CF values corroborate the results of the sensory analysis. Also, it seems that there is a maximum in the oil quality as a function of pressure and RR. Even though some experiments resulted in concentration of oxygenated compounds close to that defined as the best, from the industrial point of view it is accepted that the sensory analysis together with the CF is the final answer to this question. Indeed, it is difficult, if not impossible, to indicate general and definite limits for the physicochemical properties of concentrated oils because these properties depend on the

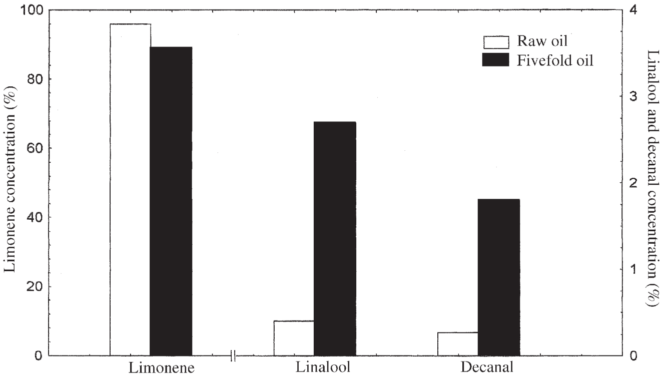

FIG. 1. Comparison of a fivefold oil (run 4, second experimental design: 80°C, 20 mbar, and 0.75 reflux ratio) obtained from vacuum distillation with raw orange peel oil with regard to the most important compounds.

TABLE 3
Results for the Vacuum Distillation of Orange Peel Oil for the Second Experimental Design (constant fivefold and T = 80°C)[a]

Run	P (mbar)	RR	Oxygenates (%)	CF	Aldehyde total (%)	Sensory analysis
1	30	0.75	3.22	5.65	6.03	Worst
2	30	0.50	3.51	6.16	6.08	Worst
3	30	0.25	3.40	5.96	6.16	Worst
4	20	0.75	4.52	7.93	7.37	Best
5	20	0.50	3.86	6.77	6.88	Worst
6	20	0.25	4.11	7.21	7.95	Intermediate
7	10	0.75	3.85	6.75	6.47	Intermediate
8	10	0.50	4.34	7.61	7.63	Best
9	10	0.25	4.31	7.56	7.68	Intermediate

[a] See Table 1 for abbreviations.

TABLE 4
Quantitative Composition (%) of Concentrated Orange Peel Oil by Vacuum Distillation for the Second Experimental Design (constant fivefold and T = 80°C)[a]

	Experiment								
Compound	1	2	3	4	5	6	7	8	9
α-Pinene	—	—	—	—	—	—	—	—	—
β-Pinene	—	—	—	—	—	—	—	—	—
Sabinene	—	—	—	—	—	—	—	—	—
Myrcene	0.14	0.10	0.13	0.15	0.13	0.13	0.09	0.12	0.11
Limonene	92.09	91.43	91.61	89.10	90.15	89.59	90.60	89.31	89.70
Phellandrene	0.21	0.22	0.22	0.20	0.21	0.20	0.21	0.20	0.21
γ-Terpinene	0.05	0.05	0.05	0.06	0.05	0.04	0.06	0.05	0.06
ρ-Cimene	—	—	—	—	—	—	—	—	—
Octanal	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Nonanal	0.24	0.26	0.23	0.25	0.33	0.37	0.35	0.23	0.34
Citronellal	0.25	0.26	0.26	0.34	0.30	0.32	0.29	0.33	0.31
Decanal	1.31	1.41	1.37	1.81	1.59	1.69	1.53	1.77	1.69
Linalool	1.91	2.10	2.03	2.71	2.27	2.42	2.32	2.57	2.62
Octanol	0.10	0.11	0.11	0.13	0.12	0.12	0.12	0.13	0.13
Neral	0.18	0.19	0.18	0.24	0.21	0.23	0.20	0.23	0.22
α-Terpineol	0.28	0.30	0.30	0.39	0.35	0.38	0.33	0.37	0.38
Geranial	0.41	0.44	0.43	0.57	0.49	0.53	0.47	0.55	0.53

[a] See Table 3 for experimental parameters.

degree of concentration and on the relative proportions of oxygenated constituents originally present (8).

ACKNOWLEDGMENTS

The authors would like to thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for the financial support and gratefully acknowledge Citrosuco S.A. for providing the orange peel oil and performing the sensory analyses.

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[Received April 9, 2001; accepted July 24, 2001]