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THE EFFECT OF RAW MATERIAL PREPARATION ON THE SUPERCRITICAL FLUID EXTRACTION OF THE OIL FROM ORANGE PEEL

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ABSTRACT

The objective of the work described in this paper was to specifically examine the effect of raw material preparation on the extraction of orange oil from orange peel by Supercritical Fluid Extraction (SFE) using a bench scale system.

Thus, experiments on fresh diced peels over ranges of pressure ranging from 80 bar to 330 bar and temperatures ranging from 30°C to 80°C gave oil yields of only up to 0.22% with highest yields being at the higher extraction temperatures. Compositions of the quality defining components were also low with the highest limonene content being 21.8% at 230 bar and 40°C. Experiments on the milled product after drying half peels gave rise to much higher yields with up to 2.6% at 280 bar and 30°C. When the half peels were shredded and then dried before extraction the oil yield was rather lower at 0.75%. Compositions of the quality defining components were much higher using the milled material with limonene contents being in the range 85% to 92% at the preferred operating conditions.

Orange peel is composed of two layers, the outer flavedo (which contains the bulk of the oil), and the inner albedo. In the third series of experiments the albedo was separated from the flavedo after which SFE was carried out on the wet diced materials and the diced and dried materials. When extracting from the flavedo at 280 bar and 30°C the yield was higher at 3.2% for dried material and 0.9% for wet material. Chemical analysis showed the limonene content to be ~90% in both cases. As expected the albedo had lower yields 0.4% for dried material and 0.1% for wet material with much lower limonene contents at 21% and 4% respectively.

It is concluded that the most appropriate process for extraction the essential oil from orange peels is to dry half peels and mill before extraction. The best operating conditions were identified to be 280 bar pressure and 30°C. Separating the flavedo from the albedo followed by drying and milling the flavedo prior to extraction will give higher yields of oil with a good quality profile, but this would be difficult to achieve in operating practice, and there would still be oil loss by dumping the albedo.

INTRODUCTION

The orange oil industry worldwide has been reported to have an annual turnover of approximately US$2b [1]. The leading producers are Brazil and the USA with Brazil recognized as the foremost producer [2]. The fruit is processed into several products such as juices, frozen concentrates and pectin; however the main product is the orange juice.

Orange peel is a by-product of orange juice production from which the essential oil is extracted. This is a valuable component being an important raw material in the food, pharmaceutical, cosmetic and perfumery industries [3]. The oil is used directly, or it may be further processed to isolate key components increasing the concentration of significant flavor and fragrance principles. Various technologies are employed in the extraction of the essential oil from orange peels, each providing differences in yield and quality of the extract. Steam distillation, solvent extraction and cold expression are some of the common industrial processes by which the oil is extracted. Each of these procedures has a major drawback which affects the yield and quality of the oil. For instance during steam distillation, the relatively high temperatures employed result in the breakdown of oil components. In the case of solvent extraction, a major concern is the inability to completely remove all of the solvent from the oil after extraction. The process of cold compression in comparison to steam distillation produces oil of superior aroma. However, the unavoidable increase of temperature due to mechanical friction causes some thermal degradation of the oil.

Supercritical Fluid Extraction (SFE) using carbon dioxide at high pressures circumvents most of the drawbacks encountered in the conventional processes, as it is carried out at close to ambient temperature and when the pressure is reduced, all of the carbon dioxide flashes off leaving uncontaminated essential oil.

There have been a relatively few published papers of the SFE of the essential oil from citrus peels; specifically from mandarin peels [4], bergamot peels [5], the baina variety of *Citrus sinensis* [6] and naveline cultivars [7]. In the case of the extraction of the essential oil from the naveline cultivar, Mira et al [7] used dried peels at pressures from 80 to 280 bar and temperatures from 20^{o}C to 50^{o}C. They did investigate the effect of particle size, concluding that particle sizes below 2mm were adequate for rapid extraction. Limonene was the main component extracted (99.5%) at 125 bar and 35^{o}C. The optimum for extracting linalool was 80 bar and 35^{o}C, similar to the result previously obtained by Temelli et al [8]. The effect of bed height was investigated by Berna et al [9], and the use of SFE was compared with ultrasonic extraction by Xhaxhiu and Wenclawiak [10].

Previous work described above basically did not investigate whether pre-drying was necessary prior to extraction and if so, if the mode of pre-drying affected the extraction process. In addition, the work did not recognize that the oil is mainly secreted in the outer skin of the peel, the flavedo, with little or no oil in the pith, referred to as the albedo.

The objective of the work was therefore to investigate the effect of pre-drying with a view to identify the most appropriate drying conditions, and also to look more closely at the distribution of the oil within the peel to evaluate if further material preparation would improve extraction efficiency. In carrying out the work the specific application to a potential commercial operation was always preeminent.

MATERIALS AND METHODS

The oranges (*citrus sinensis (*lin) Osbeck) used in this study were of the Parson Brown variety. At maturity they were handpicked and supplied from a local orchard. The oranges were initially cut into halves with a sharp knife and the juice extracted using an Oster Citrus Juicer.

Material Preparation

In the extraction experiments using fresh peels, the orange peel halves were diced into 3mm cubes using a Hobart Model FP100 Food Processor before charging to the extractor.

In the preparation of the peels for drying prior to extraction, a number of size reduced presentations were tested from drying half peels to shredded peel. Drying was carried out in an Environette fan blown Oven Drier (Cat no 700 AHS), with drying temperature ranging from 40^{o}C to 60^{o}C.

In the experiments whereby oil was extracted from the separated flavedo and albedo a hand vegetable peeler was used to carry out the separation.
Moisture contents were measured by the Dean and Stark method: AOAC method 926.12

Supercritical Extraction Apparatus

The extraction experiments were carried out in an Applied Separations Spe-ed Supercritical fluid Model 7010 extractor using carbon dioxide as the extracting fluid.

Oil Composition

The composition of each extract was measured using a Hewlett-Packard Model 5890 Series 11 Gas Chromatograph equipped with a hydrogen/air burning flame ionization detector (FID). In determining the compositions comparisons were made with the following standards: limonene, octanal, linalool, octyl acetate, decanal, decanol, neral, geranial, and geranyl acetate.

EXPERIMENTAL RESULTS

Extraction from Fresh Peels

Extractions from fresh peels were carried out over a range of pressures in the range 80 to 330 bar at a temperature of 40^{o}C, and a range of temperatures from 30^{o}C to 800^{o}C at 280 bar pressure. The moisture content of the wet peels was ~59.0% w.b.

Results obtained for the undried diced peel over the range of pressures, showed the yield to increase from 0.11% at 80 bar to 0.19% at 330 bar with extraction time of around 150 minutes. When varying temperature, the yield was 0.18% at 30^{o}C dropping off to 0.13% at 40^{o}C before rising steadily to 0.22% at 80^{o}C.

In terms of quality only 3 components were identified namely limonene, linalool and decanal. When the pressure was varied at 40^{o}C, the measured limonene content was ~1% at 80 bar rising to a peak of 21.8% at 230 bar then falling off to 5.2% at 330 bar. Linalool showed a similar trend being ~ 0.4% at 80 bar rising to its peak of 4.1% at 230 bar then dropping off to 0.6% at 330 bar.

Extraction from Dried Peels

In order to determine the most favourable drying conditions to prepare the orange peel for extraction, a series of drying experiments were carried out on half peels and shredded peel to determine the drying times and to compare extraction characteristics of the milled dried half peels and dried shredded material. These drying experiments were carried out over a range of temperatures ranging from 40^{o}C to 60^{o}C and, as expected, the drying times to bring the moisture contents down to ,<10% w.b. were a function of drying temperature, with the half peels taking longer than the shredded peels. Details on these experiments have been presented elsewhere [11], but typically at 55^{o}C, the half peels took 25hrs to reach 10% w.b. and the shredded peels 5.2hrs. Since it was deemed likely that the shredded material may lose oil during drying because of its smaller size and higher surface area, supercritical fluid extraction experiments at 300 bar and 40^{o}C were carried out on the two products to ascertain if this was so. The dried half peels were milled before charging to the extraction vessel, but the shredded material was charged without further processing. Final yields are shown in Table 1 below:

Table 1 – Extraction Yields from Dried Milled Half Peels and Dried Shredded Material

Source of Material	Extraction Yield %
Half Peels	1.56
Shredded	0.75

It was clear that, notwithstanding the significant reduction in drying time for shredded material, it is seen that about half the oil is lost during drying, so it was deemed appropriate to use milled dried half peels as the raw material for the extraction experiments on dried peels.
Extraction experiments were thus carried on the milled dried peels over the same ranges of pressures and temperatures as the wet peels i.e. 80 to 130 bar at 40ºC, and 30 to 80ºC at 280 bar. Sieve analysis gave a mean particle size of ~340 microns. The moisture content of the dried peels was ~6.0%. Extraction times were roughly half those for wet peels and the yield were much higher as seen in Table 2 below;

Table 2 – Extraction Yields from Dried Milled Half Peels over Ranges of Pressure and Temperature

Pressure in bar	Temperature in ^{o}C	Extraction Yield %
80	40	0.46
130	40	1.33
180	40	1.60
230	40	2.07
280	40	2.41
330	40	1.67
280	30	2.59
280	50	0.90
280	60	1.00
280	70	0.77
280	80	0.82

Reference to Table 2 illustrates that the highest yields occur at 280 bar pressure at the lower temperatures.
In terms of quality, as in the case of extraction from wet peel, whereas all of the 9 components tested for were present, the 4 major components were limonene, octanal, linalool and decanal with the composition of the extract at 280bar and 30ºC having the highest values as shown in Table 3.

Table 3 - Composition of Extract at 40ºC and Varying Pressures

Component	180 bar -40ºC	230 bar-40ºC	280 bar-30ºC
Limonene	88.7%	91.7%	85.4%
Octanal	0.22%	0.18%	7.3%
Linalool	1.6%	1.4%	0.9%
Octyl Acetate	0.03%	0.02%	0.01%
Decanal	0.5%	0.5%	0.3%

Extractions from Separated Flavedo and Albedo

Because it is likely that the bulk of the essential oil is in the flavedo, experiments were carried out to confirm this suggestion and to try to quantify the distribution. All experiments were carried out under the preferred conditions identified in the previous sub-section, namely 280 bar and 30ºC, the final yields being detailed in Table 4:

Table 4 – Extraction Yields from Separated Flavedo and Albedo

Peel Components	Total Oil Yield %
Wet Diced Flavedo	0.87
Dried Milled Flavedo	3.17
Wet Diced Albedo	0.11
Dried Milled Albedo	0.41

As in the case of extraction from the whole peels all 10 of the components tested were present. The percentage compositions of those having the highest values are detailed in Table 5:

Table 5 – Compositions of Exracts from Flavedo and Albedo

Component	Dried Milled Flavedo	Wet Diced Flavedo	Dried Milled Albedo	Wet Diced Albedo
Limonene	89.5%	89.2%	21.5%	4.2%
Octanal	0.17%	0.2%	n.d.	n.d.
Linalool	2.2%	2.3%	2.8%	1.0%
Octyl Acetate	0.06%	0.04%	0.05%	n.d.
Decanal	0.57%	0.42%	0.93%	0.30%

Reference to Table 5 shows the flavedo to contain high values of the quality components, the values in the albedo being much lower.

DISCUSSION

It is clear from the results on wet peels that, not only is the extraction rate low but the concentrations of the valuable components is also much lower than that of the milled dried peels. In addition, when converting the yields to a dry weight basis for direct comparison the yield from the dried milled peels is 6 times that of the wet peels.

It has been established that notwithstanding the reduction in drying time and hence reduction in drying costs, drying half peels and then milling rather than drying shredded peels before extraction is preferred because the extraction yield is doubled. In choosing the most appropriate conditions for extraction from milled dried peels the results showed that the preferred conditions are 280 bar pressure and 30^{o}C from the point of view of both yield and composition.

When compared with previously reported results, preferred conditions were for similar extraction temperatures but higher pressures.

Reference to Table 4 shows both the flavedo and the albedo to have higher yields when the materials are pre-dried even when converted to a dry weight basis. In addition, it is seen that the flavedo has 7 or 8 times more oil than the albedo. This seems to indicate that in an industrial operation it may be preferable to try to separate the flavedo from the albedo prior to drying but this would be difficult on a commercial scale.

CONCLUSIONS AND RECOMMENDATIONS

It may be concluded that the preferred process to manufacture the essential oil of orange peel by SFE would be to cut the peels in half, dry at around 50^{o}C and mill prior to extraction. Suggested extraction conditions are 280 bar pressure and 30^{o}C.

Further work on the possibility of easily separating the flavado from the albedo before drying, milling and extraction may be worthwhile.

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