(3), reported in this current paper, stimulated interest in and led to an improved colorimetric method for furfural. Furfural content can be used as an index of flavor deterioration in processed citrus juices during storage.

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POTENTIAL BY-PRODUCTS FROM WASTE CITRUS PEEL EMULSION

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Abstract. **Waste Valencia orange and grapefruit peel emulsions from citrus oil recovery units were evaluated as potentially valuable clouding agents for beverage concentrates where peel character might be desired. Initial cloud and cloud stability during extended centrifuging were similar to those for juices and pulp-wash suspensions. Cloud of orange emulsion which had been concentrated 20-fold, then reconstituted, was 70% of original; but ultrasonic treatment of concentrate increased this to about 80% by redispersing particle agglomerates. Twelve-fold grapefruit emulsion (3.5° Brix) retained more than 80% of initial cloud after reconstituting. Freezing the concentrates had no effect on cloud retention after reconstituting. Both concentrates retained some characteristic peel aroma and bitter flavor.**

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References to specific commercial products do not constitute endorsement.

The authors acknowledge with appreciation the assistance of G. P. Gerow and Barry Anderson of FMC Corporation, Lakeland, Florida, in procuring emulsion samples.

Introduction

For fruit drinks, demand for natural clouding agents, such as suspensions recovered from counter-current washing of pulp from juice finishers, has recently accelerated because of restrictions on use of brominated vegetable oil (BVO) in formulating cloud emulsions (8). The color and turbidity characteristics of waste citrus peel emulsions suggested their potential as natural clouding agents for fruit drink concentrates. This new use for waste peel emulsions might increase their value by opening new and more valuable markets, particularly in Europe.

Fruit drink concentrates made from whole fruit "squashes" have been popular for many years in Great Britain and Europe. They retain much of the characteristic aroma and taste of citrus peel. These concentrates contain at least 25% natural food parts, 80% of which may be peel constituents with very little juice (4). Such concentrates are somewhat bitter. They are generally stored unrefrigerated and prepared as drinks by mixing one part concentrate with three or four parts water. Thus, these reconstituted drinks generally contain 5 to 10% natural material derived from fruit.

Waste peel emulsions are available in quantity from two sources: 1) de-oiled waste effluent from d-limonene distillation units, and 2) centrifuge effluent from oil mills. Such effluents are quite turbid, retain their fruit color, and contain a low level of soluble solids (1-4° Brix). Centrifuge effluent also contains up to 2% residual peel oil, which may be recovered by steam stripping (10). Both effluents are usually concentrated and used in animal feed.

Natural cloud particles tend to settle during storage, in contrast to BVO-formulated emulsions stabilized by adjusting specific gravity of emulsion droplets to that of the suspending medium. Development of new sources of natural clouding agents would be aided by better methods of characterizing their cloud-settling behavior. Reproducible measures of both initial cloud and cloud stability during storage would be useful.

Suspended particles in the range of about 1-100 microns would be expected to follow Stokes' Law for settling in either a gravitational or centrifugal force field as shown below for the settling velocity of spherical particles (1):

$$V = \frac{\Delta\rho D^2 A}{18\mu} \qquad \text{(Equation 1)}$$

Where: V = Particle velocity, cm/sec
$\Delta\rho$ = Density difference between particles and fluid, g/cm³
D = Particle diameter, cm
μ = Viscosity of the suspending fluid, g/cm-sec
A = Field acceleration (g for gravity settling or RCF x g for centrifugal separation), cm/sec²
RCF = Relative centrifugal force.

Natural clouding agents must be concentrated to reduce shipping costs, but they must retain most of the original cloud after reconstituting. This study was carried out to assess cloud behavior and evaluate methods of improving cloud retention of de-oiled peel emulsions after concentrating and reconstituting. Extended centrifugation was used to approximately simulate cloud stability during settling for a few weeks.

Materials and Methods

Sample Materials

De-oiled 1.8° Brix Valencia peel emulsion (waste effluent from a d-limonene recovery system) was obtained from a citrus processing plant. Most of the oil had been stripped by superheating to about 250°F under pressure and rapidly expanding under high turbulence to atmospheric pressure. The waste effluent was cooled rapidly to about 140°F and stored under refrigeration until it could be processed (about 2 months).

Grapefruit centrifuge effluent, including desludger solid and liquid waste, was also obtained from a processing plant. This effluent (3.5° Brix and 0.3% oil) was de-oiled in a vertical tube contactor (2-inch i.d. x 91-inch height) with a steam injector at the base (3). The centrifuge effluent was preheated to about 212°F in a tubular heat exchanger at 0.5 gpm (30 sec residence time) and steam was injected to provide about 8% vaporization during two-phase co-current flow (1 min residence time). Samples of the steam-stripped effluent were stored at 35°F for several months before evaluating.

Both de-oiled emulsions had been processed under pasteurizing conditions (time and temperature), which prevented enzymatic or bacterial deterioration during storage.

Various commercially available juice and drink samples were evaluated for cloud stability by centrifugation for comparison with de-oiled emulsions. Bottled reconstituted FCOJ (12° Brix) and canned sweetened grapefruit juice (12° Brix) were procured locally. Material elutriated from citrus pulp (6.5° Brix) was obtained from a citrus processing plant. Two citrus-flavored drink concentrates, 48° Brix orange and 51° Brix lemon, were procured from Europe. These drink bases had been formulated to contain 5-10% natural fruit components and flavoring compounds in the prepared drink. The remainder was sugar, citric acid, cloud stabilizer, a preservative and water.

Concentrating and Reconstituting

Stored de-oiled orange emulsion was resuspended and centrifuged at 2 gal/min feed rate and 7500 RCF (Model SA7 Westphalia Centrifuge, Centrico, Inc., Englewood, N. J.) to remove large cloud particles, pasteurized in a tubular heat exchanger (200°F for 28 sec), and concentrated 20-fold (37° Brix) in a pilot plant falling-film evaporator (21°C and 19 mm Hg).

Laboratory samples of de-oiled orange emulsion or grapefruit effluent were centrifuged (10 min at 470 RCF) and concentrated at 60°C and 100 mm Hg in a rotary evaporator.

Emulsion concentrates were reconstituted to original concentration of cloud particles on a volume basis with water or aqueous sucrose solutions. Cloud suspensions were prepared at both 48° and

12° Brix to evaluate short-term storage stability in fruit-drink formulations.

Cloud Stabilization

Before concentrating de-oiled orange emulsion, laboratory-grade gum arabic was added at a level (0.05%) which would not significantly increase viscosity of the concentrate.

Ultrasonic treatment (Model W-185C Sonifier, Branson Instruments, Inc., Danbury, Conn.) was evaluated for improving the cloud dispersion of concentrated emulsion by treating 400 gms for 2 min at 125 watts ultrasonic power.

Flavor Tests

Samples were tasted informally by three experienced tasters and judged for overall flavor characteristics.

Physical Measurements

Viscosity of concentrated orange emulsion was measured with a Brookfield Viscosimeter (Brookfield Engineering Laboratories, Stoughton, Mass.) using a number-3 spindle.

Cloud density was measured as optical density (O.D.) of suspensions which had either settled for up to 4 months or been centrifuged under carefully controlled conditions. A Lumetron Model 401 Colorimeter (Photovolt Corporation, New York, N.Y.) equipped with a 650 nm filter was used for measuring O.D. in a cylindrical tube (18 mm O.D. x 15 cm length). Instrument reproducibility was verified by periodic measurements of O.D. of bentonite suspensions (O.D. = 0.604 at 3.0 gm/1 and O.D. = 0.958 at 6.0 gm/1) (9).

Accelerated cloud-settling conditions were approximated by centrifuging (Model UV, International Equipment Co., Needham Heights, Mass.), using 50 ml tapered tubes (29 mm O.D. x 13.3 cm length). The average radius during centrifuging was 12.5 cm. Speeds 800 to 3400 rpm were used and RCF calculated by the following equation (1):

$$RCF = 1.117 \times 10^{-5}\, rN^2$$

Where: r = Average radius, cm
N = Speed, rpm (Equation 2)

The product of RCF x time of centrifuging was used in correlating cloud-stability data. Thus, the rate of change of O.D. of the suspension, was assumed to be related to the velocity of settling given by Stokes' Law (Equation 1). Therefore, the cloud remaining in suspension (measured by O.D.) should be approximately proportional to the product RCF x time of centrifuging. This product was defined as "θ = RCF x time (sec)." Time of centrifuging was corrected to account for acceleration and deceleration (1). This correction amounted to 1/3 the sum of the time required to reach desired speed and the time to stop and increased from 0.3 min at 1400 rpm to 0.8 min at 3300 rpm. Optical densities were plotted vs. $\theta \times 10^5$ using semi-logarithmic graph paper to compress the scale and better show the effect of extended times.

Results and Discussion

Cloud Stability of Stored Emulsions

Visually dense cloud in samples of de-oiled grapefruit and orange peel emulsions were retained for up to 16 weeks at 35°F. Optical density of grapefruit de-oiled waste effluent after 4 months was 0.67 and that of de-oiled orange emulsion after 6 weeks was 0.93. Settled samples were resuspended and O.D. measured after centrifuging under various conditions of time and RCF up to 1500. These data and the O.D. of the supernatant from settled emulsions are shown in Figure 1. Theoretical time equivalents for gravitational settling (days) are indicated at the top of the figure. The observation that O.D. of settled samples fell on a smooth extension of the curve for centrifuged samples suggested that cloud particles followed Stokes' Law, and cloud density as O.D. might cor-

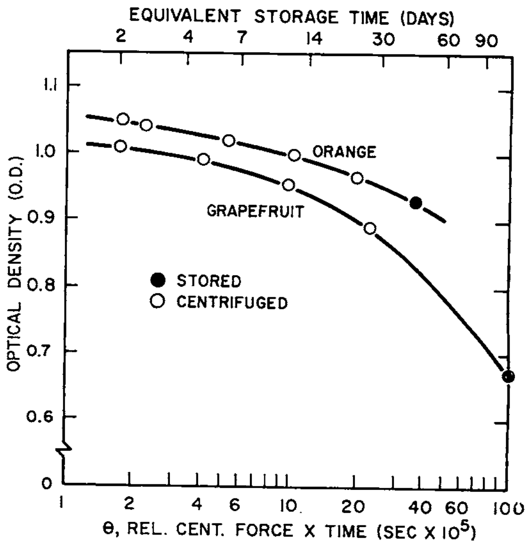

Fig. 1. Effect of centrifuging and storing on cloud of de-oiled Valencia and grapefruit emulsion.

relate with θ over a range of RCF. Thus, cloud retention of emulsions settled for 30 days (θ = 26.0 x 10^5 sec) or centrifuged at RCF = 1500 for 29 min should be approximately the same unless particle physical characteristics changed during storage by chemical or biochemical means. Four standard centrifuging conditions were chosen for accelerated settling tests to approximately simulate cloud stability behaviour after about 2, 5, 11, and 26 days' storage (Table 1). Centrifuging at 1400 rpm for 10 min corresponded approximately to the condition normally used in processing plants for determining cloud of orange juice (9).

Other Products With Natural Cloud

The accelerated cloud-stability test was applied to several citrus products to compare with results for de-oiled emulsions and to indicate the theoretical stability expected during the first month of storage (Figure 2). Reconstituted orange juice had the highest initial optical density, but, with extended centrifuging, its cloud settled at a slightly higher rate than the others. Canned sweetened grapefruit juice and orange pulp-wash suspension had similar cloud and cloud stability and were 3-4 times as high in O.D. as the 12° Brix citrus drinks. The citrus drinks had much lower cloud densities (0.2 to 0.3) but were more stable and did not settle as rapidly as juices or pulp-wash suspensions in the accelerated stability test. This illustrated the need for more dense cloud in beverage formulations to simulate appearance of natural juices.

Table 1. Centrifuge conditions.

Speed RPM	Time min	θ^z sec x 10^5	Equivalent time @ 1 g days^z
1400	10.3	1.7	2.0
3000	5.5	4.1	4.7
3300	10.7	9.7	11.2
3300	24.8	22.7	26.3

^{z}Calc. from θ = RCF x time.

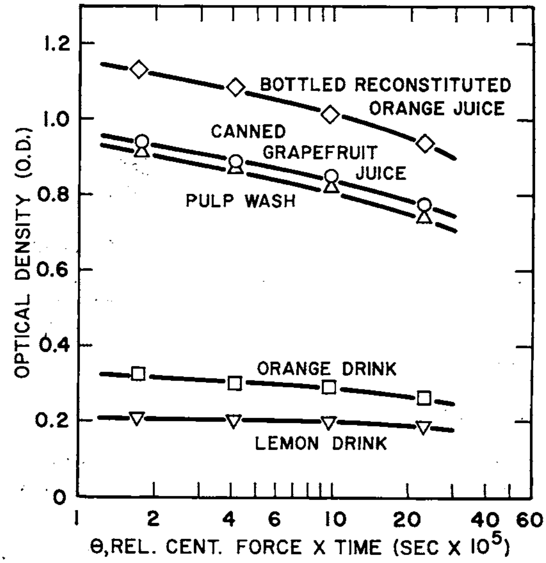

Fig. 2. Cloud stability during centrifuging various juices and drinks.

Effect of Concentrating

The effects on cloud of concentrating de-oiled grapefruit effluent 12-fold in the laboratory and reconstituting to original strength with water or 12° Brix syrup are shown in Figure 3. Some degree of particle agglomeration apparently occurred,

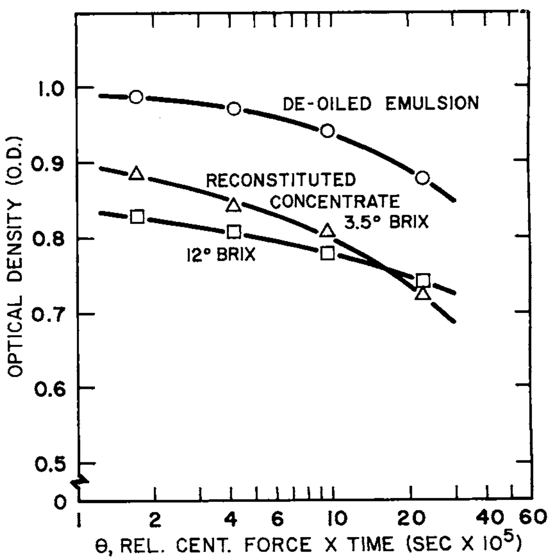

Fig. 3. Cloud stability of de-oiled grapefruit emulsion and 12-fold concentrate reconstituted in water and in 12° Brix sugar solution.

since the dispersion reconstituted in water retained only 89% of the original cloud at $\theta = 1.7 \times 10^5$ sec. The larger agglomerated particles would be expected to settle at a higher rate, resulting in lower cloud stability under more extended centrifuging conditions. This was the case as the optical density of the water-reconstituted concentrate decreased to 82% of original at $\theta = 23 \times 10^5$ sec.

Under mild centrifuging conditions the O.D. of concentrate reconstituted in 12° Brix sugar solution was lower than in water. Such apparent loss of cloud would be expected from the higher refractive index of sugar solutions at the same concentration of particles in suspension (7). Under extended centrifuging conditions, however, the 12° Brix suspension was more stable (less decrease in O.D.), because of the higher viscosity and density of the suspending medium (Equation 1).

Improving Cloud Retention

Cloud retention of reconstituted Valencia emulsion concentrate was improved by several methods. Gum arabic was added before concentrating 20-fold, and the resulting 37° Brix syrup containing 1% gum arabic had a viscosity of 600 cps at 25°C. The addition of gum arabic marginally improved cloud retention, after reconstituting to original strength with water, but had no effect on cloud stability with increasing θ (Figure 4). Gum arabic is commonly used as a cloud stabilizer at 0.1-0.2% in fruit drinks. The effects *of resuspending* to original cloud concentration in 12° and 48° Brix sugar solutions are shown in Figure 5. The 48° Brix results might approximately simulate cloud stability in a drink-base concentrate during storage. Optical density of cloud particles resuspended at original concentration in 48° Brix syrup was lower than the same concentration suspended in 12° Brix, again because of the higher refractive index. The higher density and viscosity of 48° Brix syrup improved dispersion stability considerably.

Ultrasonic treatment of Valencia concentrate increased cloud and optical density (Figure 5). Cloud retention of 20-fold reconstituted Valencia emulsion was lower than for 12-fold reconstituted grapefruit, probably caused by more agglomeration of cloud particles at the higher concentration. Freezing the concentrates at —5°F compared to storing them at 35°F, before reconstituting in water or 12° Brix sugar solution, had no effect on cloud stability.

Flavor

Both grapefruit and orange emulsions were bitter and retained some characteristic aroma of the peel, suggesting their use in products such as "squashes" in which citrus peel flavor and aroma are desired. A major contributor to bitterness may be limonin, especially in grapefruit emulsion (6).

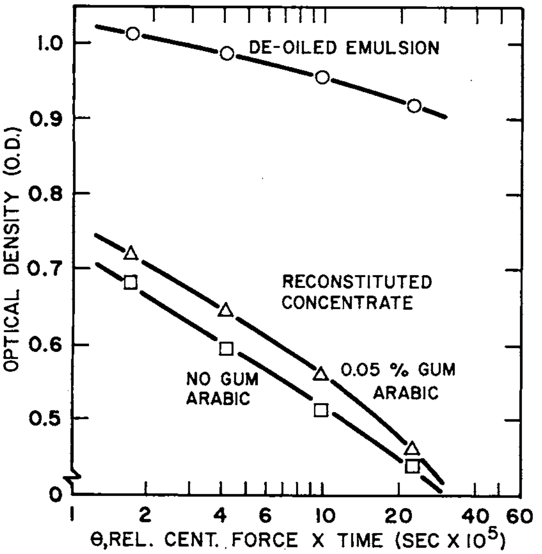

Fig. 4. Effect of gum arabic on cloud stability of 20-fold Valencia emulsion concentrate reconstituted in water.

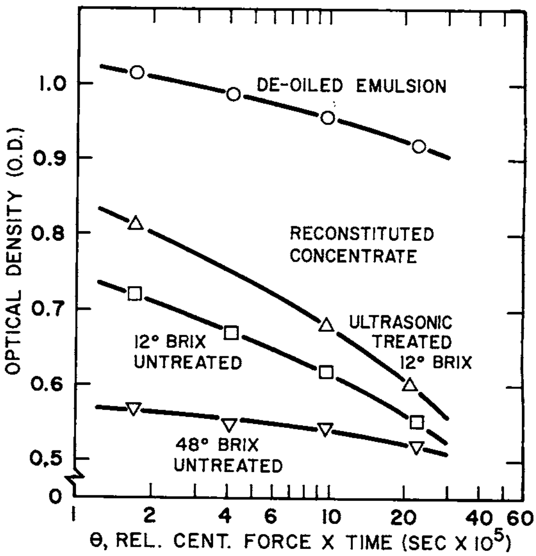

Fig. 5. Cloud stability of de-oiled Valencia emulsion and 20-fold concentrate (with 1% gum arabic) reconstituted in 12° and 48° Brix sugar solutions showing the effect of ultrasonic treatment before reconstituting.

The bitterness in grapefruit de-oiled emulsion decreased during storage at 35°F; naringen, another bitter component in grapefruit is only slightly soluble at low temperatures and may have precipitated (5). Analyses of distillates recovered during concentration of grapefruit emulsion in the laboratory showed that traces of nootkatone, a primary grapefruit flavoring constituent, continued to distill over after other volatile components had been removed. Thus, residual nootkatone probably contributed to the flavor of reconstituted grapefruit emulsion concentrate and may have contributed somewhat to bitterness (2). The nonvolatile antioxidants found in folded cold-pressed peel oil would also be retained during concentration.

Summary

Waste peel emulsion from citrus cold-pressed oil mills and the de-oiled waste effluent from d-limonene recovery units associated with these mills offer a potential source of cloud, color, and flavor for fruit drinks. Cloud stability in 12° Brix sugar solutions during extended centrifuging compares favorably with that of whole juices and pulp wash suspensions. With its low level of soluble solids, the cloud material may be concentrated to much higher levels than fruit juices or pulp wash. Cloud retention is reduced somewhat by the concentration process, but no further losses occur during freezing and thawing. Gum arabic may be used to improve cloud retention during concentrating, and ultrasonic treatment of concentrate further improves cloud. Cloud dispersions are very stable in 48° Brix sucrose solutions simulating fruit drink concentrate, where cloud stability during shelf storage is most desirable. Such drinks made from peel emulsion would retain some characteristic peel aroma and bitter flavor.

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INTERMITTENT WARMING OF GRAPEFRUIT TO AVOID RIND INJURY DURING STORAGE

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Abstract. **'Marsh' grapefruit (Citrus paradisi Macf.) increased in susceptibility to rind injury and decay during storage at 4.5°C as the season progressed. Intermittent weekly warming of the fruit reduced both chilling injury and decay. Best results were obtained by warming for 48 hr to 15.5°C and for 8 hr to 21.0°C. During a 2-wk holding period at 21.0°C following storage, ethanol in juice increased more in fruits which had been stored continuously at 4.5°C than in those receiving any warming treatment. Solids, acids, and pH were not affected by intermittent warming.**

In the prolonged storage of grapefruit, a number of problems may arise. For example, at temperatures near 0.0°C scald and watery breakdown may occur; at 4.5°C rind pitting is often prevalent; and at 10.0°C the fruits become orange colored and are subject to decay (10). A major study on the prevention of storage diseases of grapefruit by Brooks and McColloch (1) included intermittent warming, exposure to CO_2, oiled wrappers, and wax coatings. Further investigations of intermittent warming were suggested but no *action* taken until, in a recent study (6), it was found that warming of stored citrus fruits to 21.0°C for