

November, 1948

UNIVERSITY OF FLORIDA
AGRICULTURAL EXPERIMENT STATIONS
HAROLD Mowry, Director
GAINESVILLE, FLORIDA

FLORIDA CITRUS OILS
Commercial Production Methods and Properties
of Essential Oils
(1947 - 48 Season)

J. W. KESTERSON and O. R. McDUFF

TECHNICAL BULLETIN

Cooperative Project of Citrus Experiment Station and
Florida Citrus Commission

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FLORIDA CITRUS OILS

Commercial Production Methods and Properties of Essential Oils

(1947 - 48 Season)

J. W. KESTERSON¹ and O. R. MCDUFF²

INTRODUCTION

Today the processing of citrus fruits is a vast business in Florida, almost 50 million boxes of oranges, grapefruit, and tangerines having been processed commercially during the 1947-48 season. This represented approximately 55 percent of the citrus crop which was harvested. The principal and primary products which resulted from the processing of this huge quantity of fruit were canned unconcentrated and concentrated citrus juices and canned citrus sections.

Over half of the weight of the 50 million boxes of citrus fruits used by the processing industries consisted of peel, pulp, rag, and seeds. During the past 15 years an entirely new industry has developed to utilize these enormous quantities of refuse from the canneries, formerly considered waste products but now fundamental in the economy of Florida.

The essential oil, found in the peel of the fruit, is the first product recovered from cannery refuse. Oil of orange is the most useful of the citrus oils produced in Florida, and commands a price which justifies economically the operation of a plant for its recovery.

A one-year survey of the commercial production of essential oils in Florida was completed in June 1948, near the end of another citrus processing season. Methods of commercial production used throughout the state during the 1947-48 season were studied and physical and chemical properties of many types of essential oils were determined. The principal purpose of this investigation was to determine by what means essential oils of very high quality could be produced. Through the use of the data obtained, it is hoped that the citrus industry in Florida will be able to produce citrus oils which will consistently meet the specifications of the United States Pharmacopoeia

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(24)³ and also other high quality requirements of essential oil consumers throughout the country. Production of oils of highest quality and uniformity should result in a larger consumer market. Another purpose of this study was to determine the relationship between the physical and chemical characteristics of the various types of oils and such factors as methods of extraction, methods of processing, fruit variety, fruit maturity, and others.

It is realized that the results herein presented are based on the commercial production of essential oils for only one season. However, representatives of the citrus industry have cooperated readily and have shown keen interest in this work. Results of this investigation are presented now in the belief that they will be of immediate help to manufacturers now producing essential oils in Florida. A similar survey will be continued for one or two more seasons, and other factors affecting quality, such as stability and flavor, will be investigated.

REVIEW OF LITERATURE

Many investigators have pointed out that the quality of citrus oils is dependent upon many factors, some of which are soil, climate, method of extraction of the oil, weather, and maturity of the fruit.

Citrus oils are contained in oval, balloon-shaped oil sacs or vesicles located in the outer rind or flavedo of the fruit. Winton and Winton (26) describe the exact location of these oil sacs in their discussion of the microscopic structure of the flavedo of the orange. Hood (15) found a wide variation in the oil yield of Florida oranges, reporting values of 0.11 to 0.58 percent calculated on the weight of the whole fruit. He stated that the oil content does not reach its maximum until the oranges are fully mature, but is present in commercial quantities before the fruit is ready for harvest. He also noted that a decrease in oil content immediately follows a period of rainfall. Bartholomew and Sinclair (3) studied the effect of age, size, and environment on the relative amounts of oil in California oranges. Atkins, Wiederhold, and Heid (2) reported the oil content of cull Persian limes to be 0.32 percent on a whole fruit basis.

To secure the oil from the peel of citrus fruits, the oil sacs must be punctured by either pressure or rasping. Methods of

³ Italic figures in parentheses refer to Literature Cited in the back of this bulletin.

oil extraction used in Florida during the 1937-38 season were investigated by von Loesecke and Pulley (25) and they showed that the method of preparation had an effect upon the physical characteristics of the oil. However, they did not find any relation between the time of production and the physical characteristics, and reported that there were no great differences in the properties of the oil from different fruit varieties or from fruit produced in different counties. Atkins, Wiederhold, and Heid (2) extracted oil from cull limes by using both a screw and a Pipkin (22) press and the centrifuging of lime oil emulsions has been discussed by Moore, Atkins, and Wiederhold (17). Guenther (13) in a recent series of articles is reviewing methods of oil extraction used in the United States, and in foreign countries, and states that the method of oil extraction and the amount of carrier water used in a process affect the quality of the oil.

The physical and chemical characteristics of Florida orange, grapefruit, tangerine, and lime oils have been reported by many investigators (2, 5, 9, 11, 14, 18, 19, and 25). Some of these results reported are presented in Table 1, which also includes values for oils from other sources as reported by Poore (23) and Guenther (7, 9). Foote and Gelpi (5) noted variations in the properties of different lots of Floridian oil of orange and suggested that producers should unite in the blending and marketing of their oils in an effort to maintain the same quality from year to year.

Nelson (18), Nelson and Mottern (19, 20), and Markley, Nelson, and Sherman (16) have carried out investigations relative to the chemical constituents of orange, grapefruit, and tangerine oils produced in Florida.

Guenther (8) stated that Naves reported that Guinea orange oils extracted from fully matured fruit showed a higher specific gravity, refractive index, aldehyde content, and evaporation residue but a lower optical rotation than oils pressed from green fruit.

When oranges were kept in cold storage for periods longer than six weeks previous to the extraction of the oil, de Villiers (4) found an increase in the specific gravity, optical rotation, iodine number, and saponification value, but a decrease in the aldehyde content of the oil.

Fundamental information relative to all types of essential oils produced throughout the world is found in Perry (21) and Gildemeister and Hoffman (6). Guenther (12) has written the first of a series of volumes in which he is bringing the whole

TABLE 1.—PROPERTIES OF CITRUS OILS AS REPORTED BY OTHER INVESTIGATORS.

Reference	Coldpressed Orange	Florida Coldpressed Orange		California Coldpressed Orange		Other Florida Coldpressed Oils			Distilled Oils	
	U.S.P. XIII Specifications (24)	Source 1 (25)	Source 2 (5)	Valencia (28)	Navel (28)	Grapefruit (19)	Tange- rine (11)	Lime (9)	Cali- fornia Orange (7)	Florida Lime (9)
Specific gravity (25° C./25° C.)	0.842 to 0.846	0.8434	0.8425	0.8440	0.8455	0.8563 (20° C./20° C.)	0.845	0.886 (15° C.)	0.840 to 0.842	0.8632 (15° C.)
Refractive index (20° C.)	1.4723 to 1.4737	1.4726	1.4734	1.4735	1.4738	1.4758	1.4748	1.4855	1.4717 to 1.4730	1.4759
Evaporation residue %	not less than 1.7%	4.18	2.80	3.61	4.53	7 to 8	3.3	13.0	0.5 to 1	
Optical rotation (25° C.)	not less than +94° and not more than +99° in 100 mm tube	+96.49°	+95.5°	+97.78° (20° C.)	+96.93° (20° C.)	+93.28° (20° C.)	+92.5°	+41.26°	+98° to +99.1°	+43.20°
10% Distillate	Optical rotation (25° C.)	equal to original oil or not more than 2° difference	+97.55°	+97.5°	+99.21° (20° C.)	+98.71° (20° C.)				
	Refractive index (20° C.)	not less than 0.0008 and not more than 0.0015 lower than original oil	1.4719	1.4729	1.4723	1.4724				

subject up-to-date. In this first volume he ably presents information on the production, chemistry, analysis, and uses of the essential oils.

In spite of the profusion of literature there has been lacking sufficient knowledge concerning the character of oils produced in Florida. Such information must necessarily represent broad scale sampling to include the effects of varieties, season, and methods of extraction if an accurate picture of the production is to be presented. In this work the writers have attempted to produce such an accurate broad scale picture that covers the entire production in Florida, and all sampling has been carried out accordingly.

METHODS OF COMMERCIAL MANUFACTURE

COLDPRESSED OILS

General Processing Procedure.—Citrus peel oils are expressed in Florida by four different types of equipment; namely, (1) Pipkin roll, (2) screw press, (3) Fraser Brace extractor, and (4) Pipkin juice extractor. The general processing procedure, used after the extraction of oil from the peel, is very similar in most of the commercial plants. All of the above methods of extraction give an emulsion of oil and water. The oil is separated centrifugally from the aqueous phase by passing the emulsion through a sludger (8,000-10,000 r.p.m.) and then through a polisher (16,000-18,000 r.p.m.). Following separation, the oil is stored for approximately one week at 32°-40° F. and during this winterizing treatment undesirable waxy materials separate from the oil and are allowed to settle. The clear oil is decanted into stainless steel storage tanks or tin-dipped containers, which are then maintained at a storage temperature of about 40° F. Air is usually excluded from the container in order to prevent deterioration. Exclusion of air usually is accomplished either by filling the container full of oil or by displacement of the air with carbon dioxide.

Pipkin Roll Method of Extraction.—A Pipkin Roll (22) is shown in Fig. 1, and the flow and material balance sheet for this process is given in Fig. 2. In this method the oil is expressed by passing peel of the fruit between two striated rollers of stainless steel that turn in opposite directions. The distance between the two rollers is adjusted so that the pressure against the peel is just sufficient to puncture the oil cells without breaking or rasping the peel. Small striations or grooves are dis-

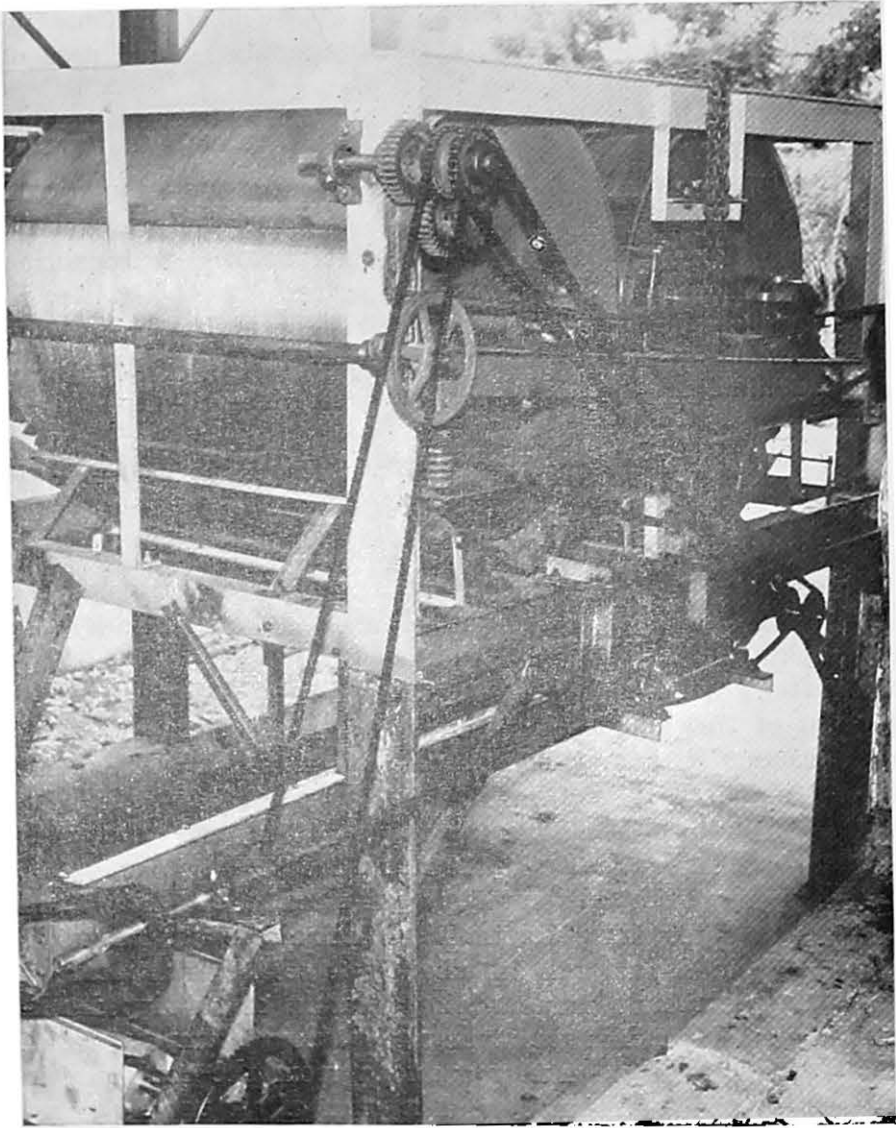


Fig. 1.—Pipkin roll. (Photograph courtesy Essential Oil Producers, Inc., Dunedin, Fla.)

tributed over the entire surface of the rolls and are of a depth sufficient to receive the oil from the oil cells, thereby keeping it out of contact with the peel and thus eliminating to some extent its absorption by the albedo of the fruit.

Screw Press Method of Extraction.—In this method tapered screws press the crushed peel against a perforated screen, thereby squeezing out the oil. This operation can be carried out with

the screws in either a vertical or horizontal position. Water may, or may not, be used in the pressing operation. Figure 3 is a flow and material balance sheet for the manufacture of coldpressed citrus peel oil by the use of screw presses.

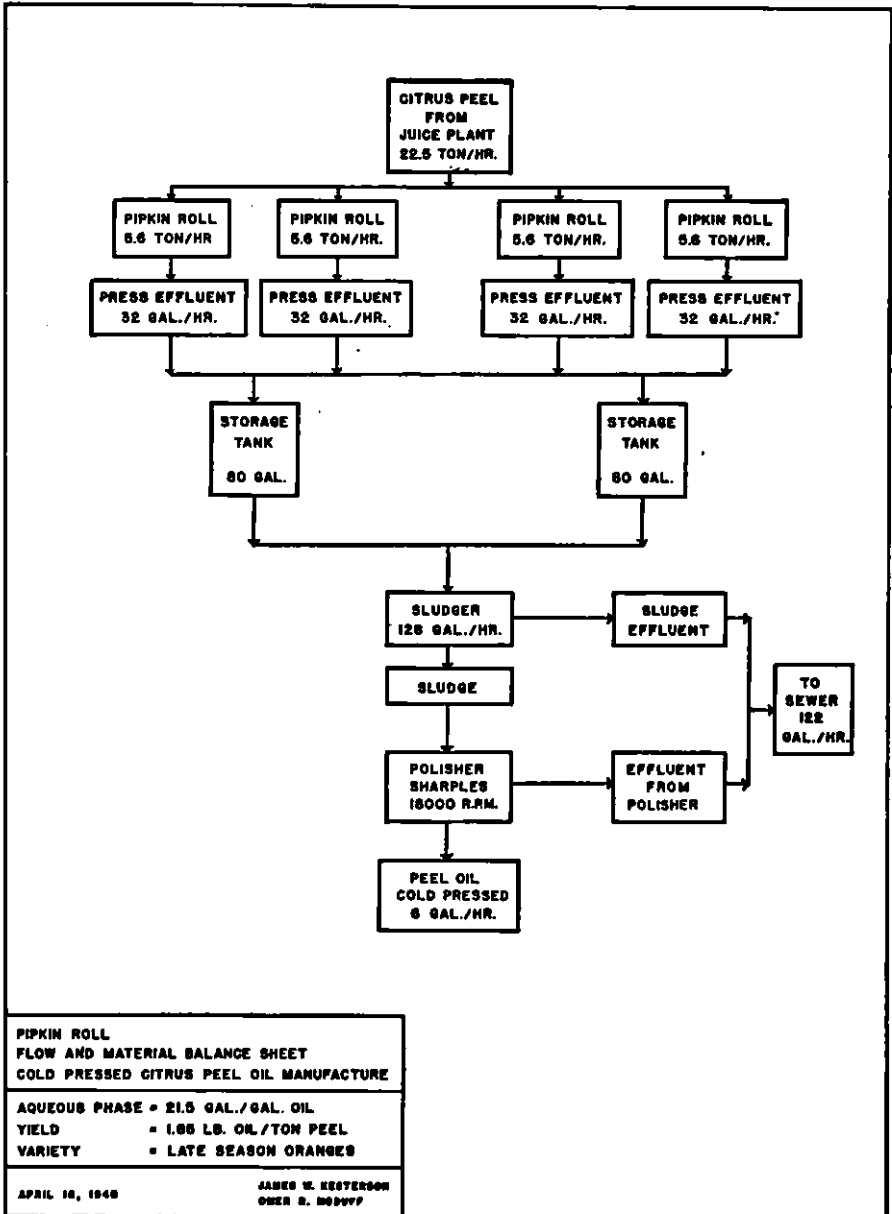


Fig. 2.—Flow and material balance sheet for process using Pipkin roll.

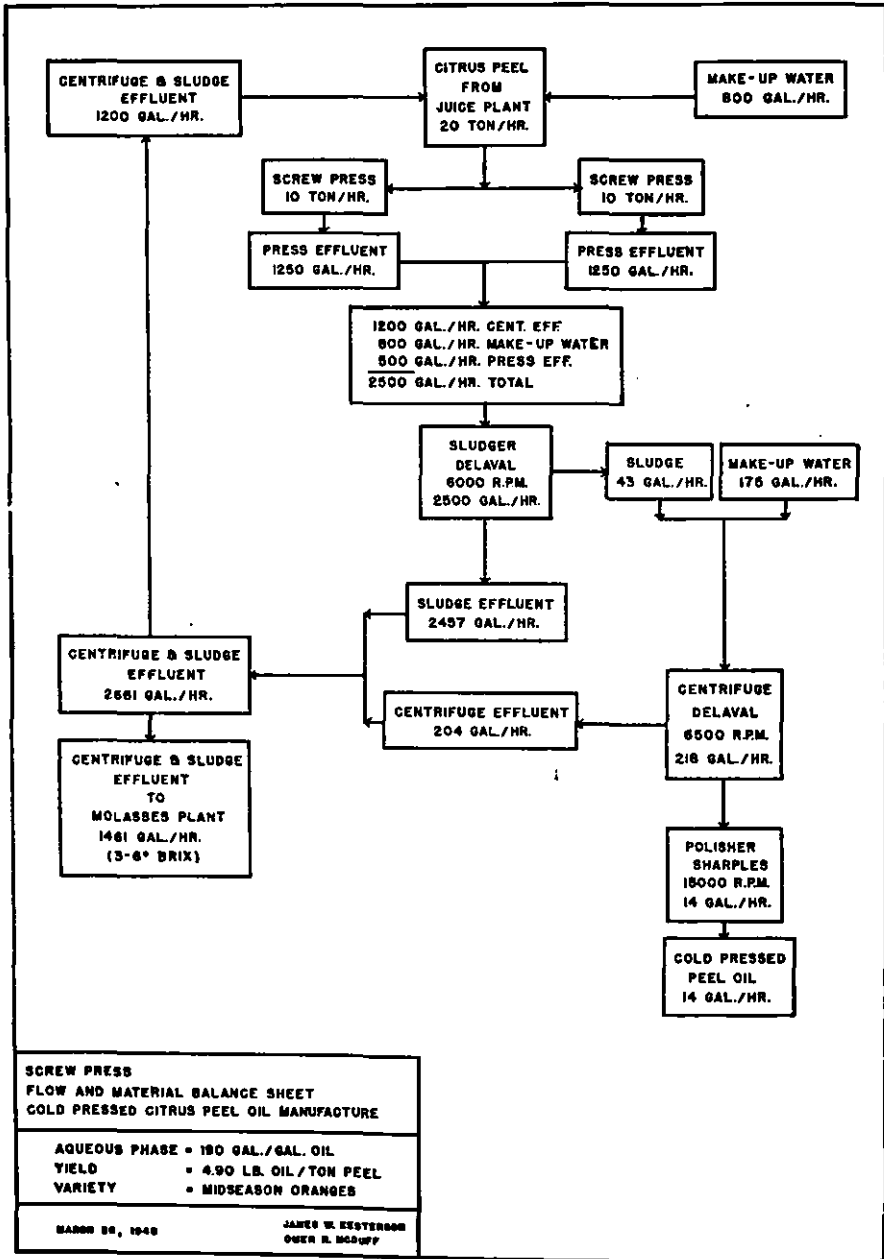


Fig. 3.—Flow and material balance sheet for process using screw press.

Fraser Brace Extractor.—Whole fruit is passed through a corridor of carborundum rolls in this process, as shown in Fig. 4. As the fruit passes through the extractor it is turned over and over and abrasive rolls rasp the flavedo from the fruit. Water

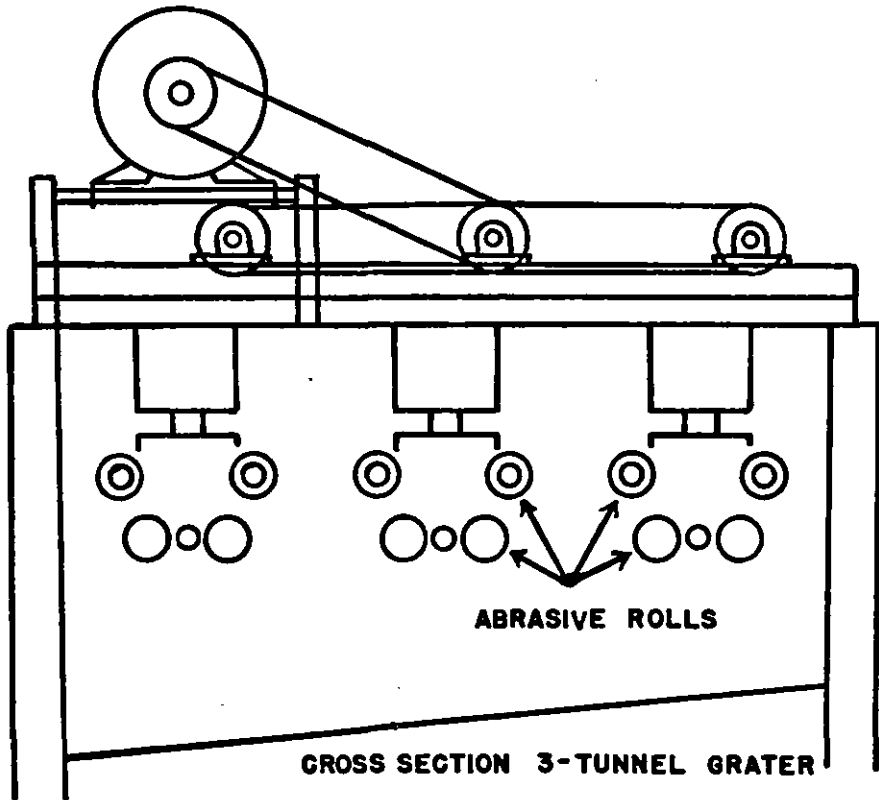


Fig. 4.—Cross-section diagram of Fraser Brace extractor. (Courtesy Fraser Brace Engineering Co., Tampa.)

sprays are directed onto the fruit and rolls to wash away the oil and grated peel. The oil and water emulsion is passed over a screen to remove the suspended solid particles and then transferred to settling tanks in which it is held from three to 12 hours to effect complete settling and to allow the emulsion to break. The machine is completely enclosed and very little loss of oil is encountered. Figure 5 is a flow and material balance sheet for this process.

Pipkin Juice Extractor.—The Pipkin Juice Extractor (Fig. 6) provides a method whereby both the juice and the peel oil from whole fruit are secured simultaneously, but in such a manner that they do not come in contact with each other to any great extent. The machine is of the rotary type and has 24 squeezing heads, which are all actuated by a common cam. The extractor is furnished complete with a feeder mechanism and a built-in electric power unit. The whole fruit is fed into a squeezing cup where just enough pressure is applied to remove all of the juice

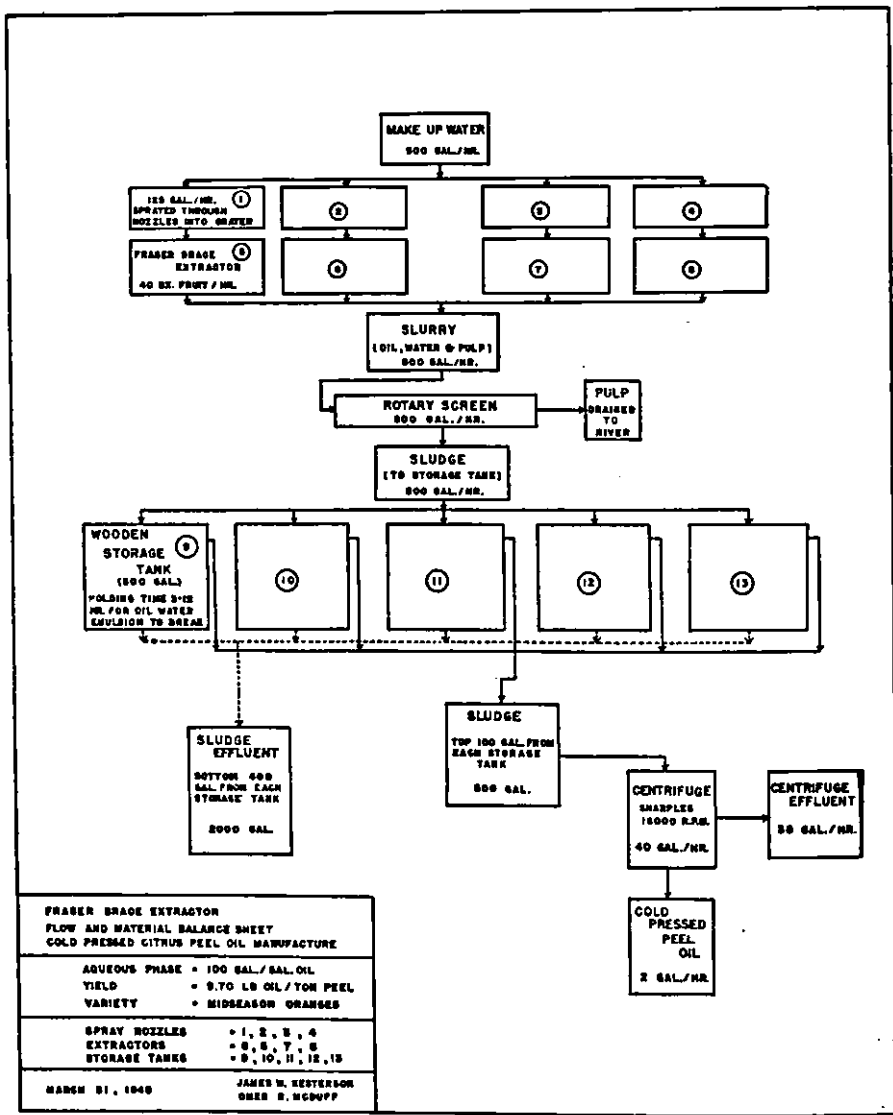


Fig. 5.—Flow and material balance sheet for process using Fraser Brace extractor.

from the fruit and at the same time rupture the oil cells. The juice and the oil emulsion are collected in separate trough assemblies. The flow and material balance sheet for this process is given in Fig. 7.

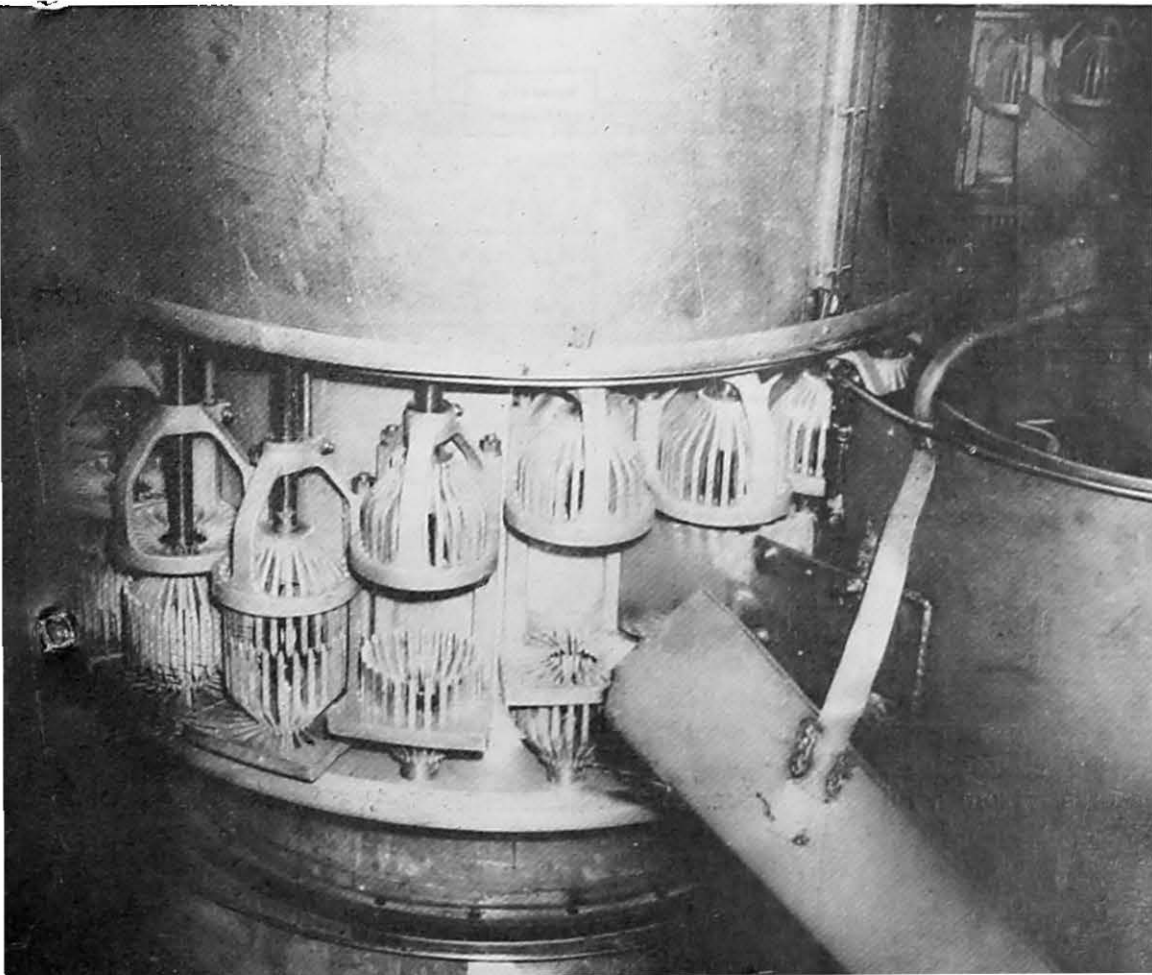
DISTILLED OILS

Distilled oil of orange, grapefruit, or tangerine is secured by some processors as a by-product in the canning of citrus fruit

juices. Some of the citrus peel oil becomes mixed with the juice as it is extracted by the various types of juice extractors used in the canneries. Excessive amounts of peel oil in the juice are detrimental to the quality of the canned juice; therefore, in most canning plants the oil content of the juice is reduced to a desirable level by passing the juice through a deoiler. The juice is usually flashed in the deoiler, which is operated under a vacuum of 11 in. (190° F.) to 25.5 in. (130° F.), and a vapor mixture of oil and water is removed. Then the mixture of oil and water vapors is condensed and the oil is separated from the condensate by decantation or centrifuging. Vacuum steam distilled oils, which are manufactured in this manner, will have slightly different properties from oils which are obtained by steam distillation at atmospheric pressure.

Stripper oils are obtained as a by-product from the manufacture of citrus molasses, which is made from the press liquor

Fig. 6.—Pipkin juice extractor. (Photograph courtesy Food Machinery Corp., Lakeland, Fla.)



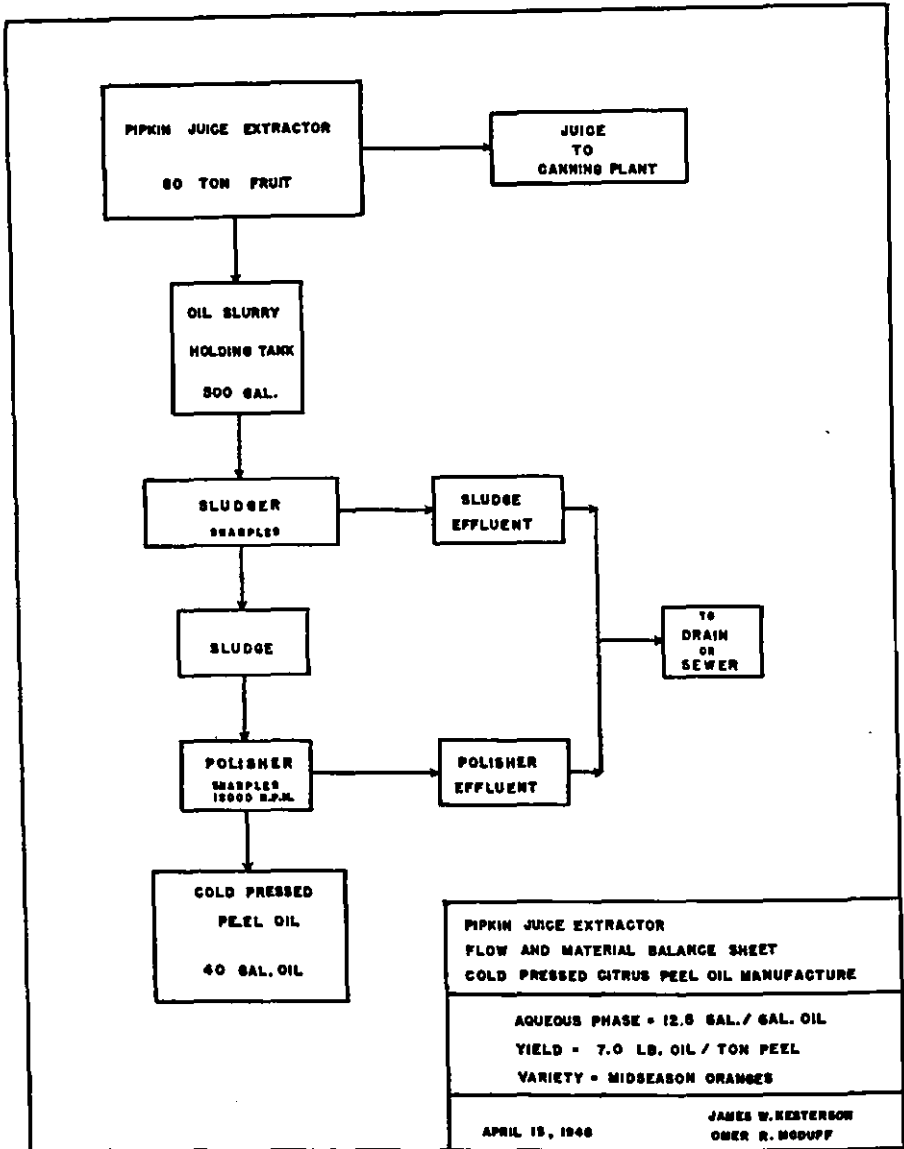


Fig. 7.—Flow and material balance sheet for process using Pipkin juice extractor.

from plants manufacturing dried citrus pulp for cattle feed. Press liquor results when limed, shredded citrus peel is pressed prior to drying. Citrus peel oil is present in this press liquor and is usually removed by heating the latter to 230° to 240° F. and then flashing at atmospheric pressure. Stripper oil is usually a mixture of citrus oils, since the press liquor is often obtained from a mixture of orange and grapefruit peel.

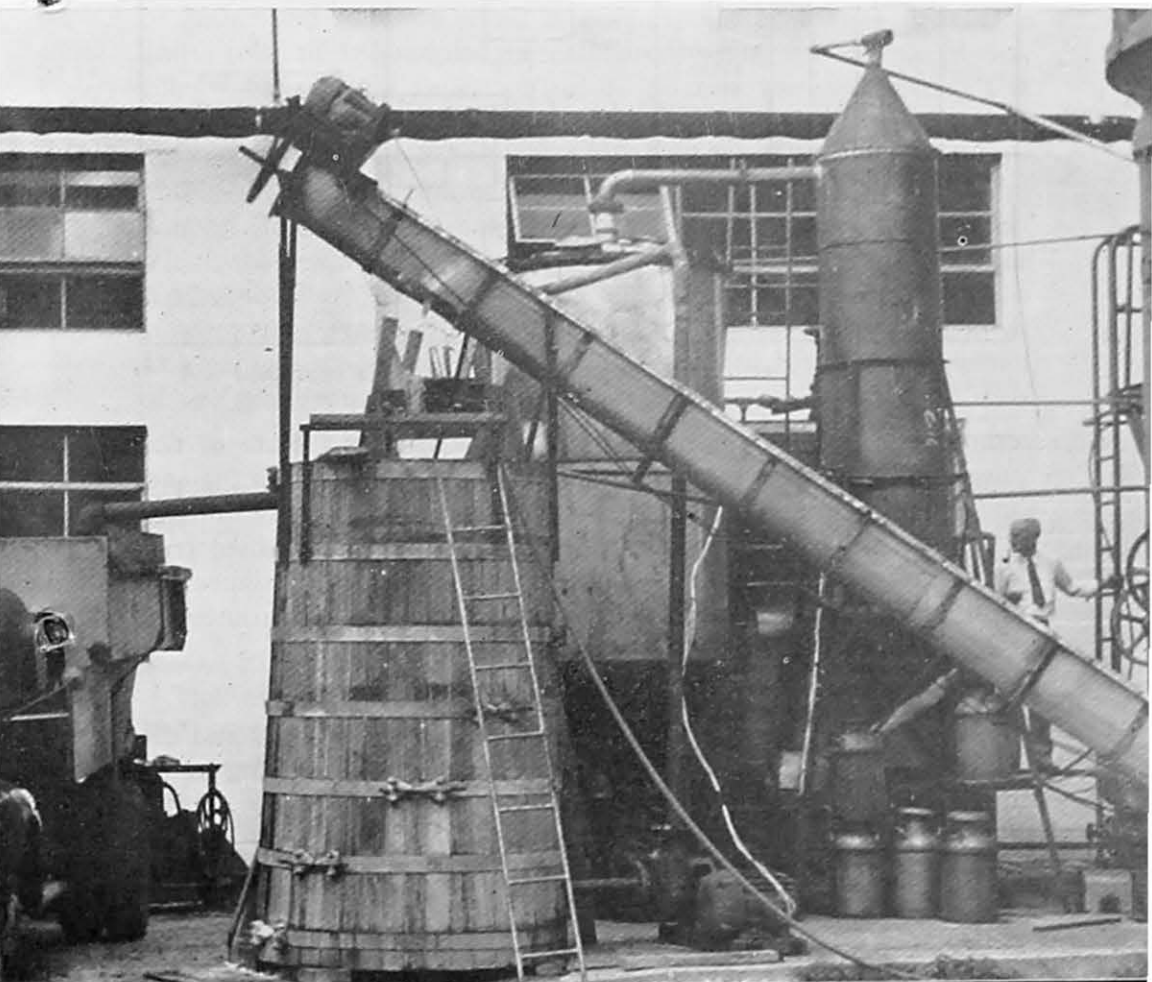
Distilled oil of lime is manufactured in Florida from cannery peel. The peel is first passed through a Pipkin roll in order to secure some coldpressed oil; then it is mashed or chopped and finally steam distilled at atmospheric pressure. Figure 8 shows an installation for the manufacture of expressed and distilled oil of lime, and the flow diagram for this commercial process is given in Fig. 9.

EXPERIMENTAL PROCEDURE

SURVEY OF COMMERCIAL PLANTS

Information pertaining to the various processes used in Florida for the manufacture of expressed and distilled citrus peel oils was secured through the helpful cooperation of commercial processors. In order to secure the data used in the preparation of flow and material balance sheets, the authors visited plants

Fig. 8.—Installation for the manufacture of Florida expressed and distilled oil of lime.



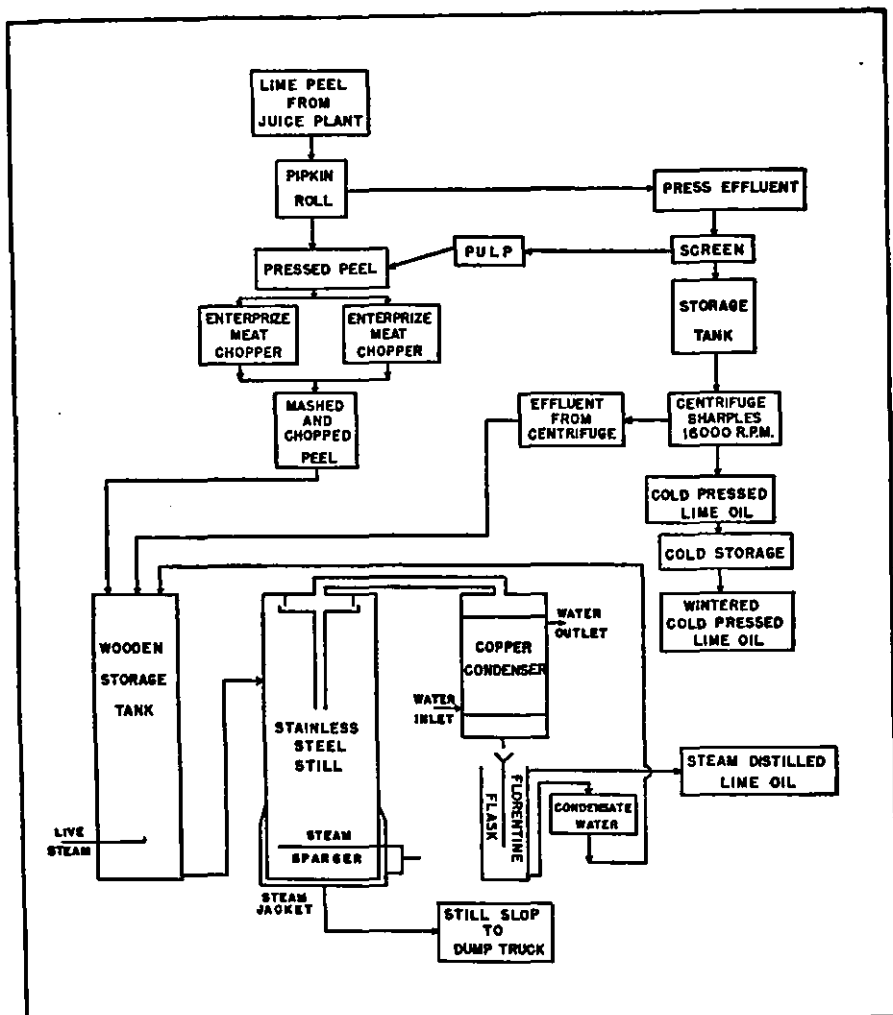


Fig. 9.—Flow sheet for the manufacture of Florida expressed and distilled oil of lime.

employing the various methods of oil extraction. Rate of flow measurements were made on each unit process operation for each individual process. Data were taken covering periods of operation of four to 24 hours' duration. Information obtained from each study was incorporated in a flow and material balance diagram for that particular process, and these are presented in Figs. 2, 3, 5, 7, and 9.

COLLECTION OF SAMPLES

A total of 83 samples of various types of coldpressed and distilled citrus oils was secured from commercial processing plants during the 1947-48 season.

Forty-two samples of coldpressed oils of orange, grapefruit, and tangerine were secured from four plants, each of which was using a different method for the extraction of the oil from the peel. These samples were taken once a month from lots of oil ranging from 500 to 11,000 pounds, which represented the production for approximately one week.

One plant furnished 12 samples of expressed orange oil, which were analyzed to determine if storage of the fruit for several days prior to the extraction of the oil would cause any change in the physical and chemical characteristics of the oil. Part of a selected lot of Valencia oranges was processed through the oil plant on the day it was picked and an equal quantity of the same lot of fruit was held in storage bins from three to five days before the oil was extracted. Each comparative set of samples was made by the same type of extractor under exactly the same conditions. These 12 samples were representative of 132,000 pounds of oil that was extracted from approximately 840,000 boxes of fruit.

Samples of distilled oils of orange and grapefruit from 250 to 350-pound batches of oil were collected from five canneries and a total of 18 samples were secured. Only one sample of distilled tangerine oil representing 35 pounds was obtained. The six samples of expressed oil of lime, the five samples of distilled lime oil, and the one sample of distilled oil from Meyer lemon were obtained from one commercial processing plant during July and August 1948. These samples represented the coldpressed oil which was expressed from 3,850 boxes of Persian limes. After the removal of the coldpressed oil, 1,100 of these boxes were subsequently steam distilled to produce the distilled oil of lime. The sample of Meyer lemon oil was secured by the distillation of the peel from 25 boxes of this fruit.

METHODS OF ANALYSES

The physical properties of the original oils and the 10 percent distillates were determined by the Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists (1). The specific gravity was determined at 25°C./25°C. and the optical rotation at 25°C. as recommended by the United States Pharmacopoeia (24).

The aldehyde content of the oils was determined by the hydroxylamine method, a standard procedure for which is given by Guenther (12). The final end point for the reaction was obtained by using a titrimeter rather than the bromphenol blue

indicator. All of the aldehyde values were calculated as decyl aldehyde, except those for the lime and Meyer lemon oils, which were calculated as citral.

The method of Seeker and Kirby as reported by Poore (23) was used for the determination of esters. In this method the aldehydes present are removed with hydroxylamine hydrochloride prior to the saponification of the esters.

The evaporation residue was determined by a method very similar to that given by Guenther (12). A watch glass (100 mm. in diameter) was used in place of an evaporating dish, and after having been heated on the steam bath for the prescribed length of time the watch glass was transferred to an oven at 100° C. and dried for one hour.

EXPERIMENTAL RESULTS
COLDPRESSED OIL OF ORANGE

The physical and chemical properties of samples of coldpressed oil of orange, which were secured from four commercial plants each month from October 1947 through May 1948, are presented in Table 2. Each of the four plants used a different method for expressing the oil. These data are also shown graphically in Figs. 10 to 15 inclusive.

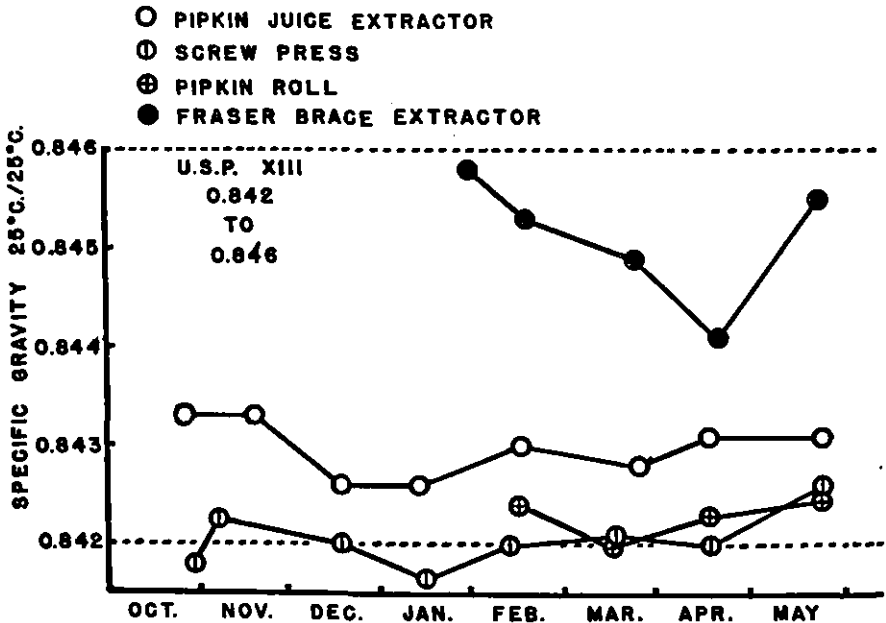


Fig. 10.—Specific gravity of coldpressed orange oils extracted by four different methods during the 1947-48 season.

TABLE 2.—THE PHYSICAL AND CHEMICAL PROPERTIES OF UNDEPRESSED ORANGE OILS PRODUCED IN FLORIDA.

Type of Extractor	Variety of Fruit*	Specific Gravity 25°C./25°C.	Refractive Index n _D ²⁰	Refractive Index of 10% Distillate n _D ²⁰	Difference	Optical Rotation α _D ²⁵	Optical Rotation of 10% Distillate α _D ²⁵	Difference	Aldehyde Content %	Ester Content %	Evaporation Residue %
October, 1947											
Pipkin juice extractor	100% H	0.8433	1.4729	1.4714	0.0015	+97.57	+97.75	0.18	1.17	0.44	2.52
Screw press	50% H 50% PB	0.8419	1.4723	1.4708	0.0015	+97.57	+97.75	0.18	1.01	0.42	2.20
November, 1947											
Pipkin juice extractor	25% H 75% P&S	0.8433	1.4728	1.4715	0.0013	+97.01	+97.05	0.04	1.31	0.38	2.59
Screw press	50% H 50% PB	0.8422	1.4724	1.4709	0.0015	+97.57	+97.60	0.03	0.92	0.30	2.02
December, 1947											
Pipkin juice extractor	10% H 50% P 40% S	0.8426	1.4725	1.4712	0.0013	+97.01	+97.06	0.05	1.63	0.33	2.18
Screw press	50% H 50% PB	0.8420	1.4723	1.4709	0.0014	+97.53	+97.60	0.07	1.34	0.48	1.77
January, 1948											
Fraser Brace extractor	50% P 50% S	0.8458	1.4733	1.4709	0.0024	+95.16	+97.12	1.96	1.08	1.45	4.81
Pipkin juice extractor	60% S 35% P 5% H	0.8426	1.4724	1.4709	0.0015	+96.81	+96.81	0.00	1.74	0.42	1.94
Screw press	50% P 50% S	0.8416	1.4721	1.4707	0.0014	+97.49	+97.52	0.03	1.55	0.33	1.38
February, 1948											
Fraser Brace extractor	50% P 50% S	0.8453	1.4734	1.4703	0.0031	+95.16	+97.12	1.96	1.08	1.50	4.93
Pipkin juice extractor	50% P 50% S	0.8430	1.4724	1.4710	0.0014	+96.81	+97.37	0.56	1.78	0.38	2.19
Screw press	45% P 45% S 10% V	0.8420	1.4723	1.4710	0.0013	+97.13	+97.54	0.41	1.41	0.20	1.68

TABLE 2.—THE PHYSICAL AND CHEMICAL PROPERTIES OF COLPRESSED ORANGE OILS PRODUCED IN FLORIDA—(Concluded).

Type of Extractor	Variety of Fruit*	Specific Gravity 25°C./25°C.	Refractive Index n _D ²⁰	Refractive Index of 10% Distillate n _D ²⁰	Difference	Optical Rotation α _D ²⁵	Optical Rotation of 10% Distillate α _D ²⁵	Difference	Aldehyde Content %	Ester Content %	Evaporation Residue %
Pipkin roll	50% P 50% S	0.8424	1.4722	1.4709	0.0013	+97.76	+97.77	0.01	1.70	0.15	1.49
March, 1948											
Fraser Brace extractor	50% P 50% S	0.8449	1.4734	1.4710	0.0024	+95.21	+96.96	1.75	1.64	0.35	3.70
Pipkin juice extractor	100% V	0.8428	1.4723	1.4708	0.0015	+96.61	+96.96	0.35	2.04	0.08	2.08
Screw press	50% P 50% P&S	0.8421	1.4719	1.4711	0.0008	+97.04	+97.24	0.20	1.52	0.04	1.95
Pipkin roll	100% V	0.8420	1.4718	1.4708	0.0010	+97.34	+98.19	0.85	1.98	0.34	1.07
April, 1948											
Fraser Brace extractor	100% V	0.8441	1.4730	1.4713	0.0017	+96.10	+97.61	1.51	1.65	0.97	3.12
Pipkin juice extractor	100% V	0.8431	1.4725	1.4712	0.0013	+96.19	+97.21	1.02	1.97	0.53	2.09
Screw press	100% V	0.8420	1.4722	1.4711	0.0011	+96.69	+97.25	0.56	1.52	0.53	1.71
Pipkin roll	100% V	0.8423	1.4721	1.4711	0.0010	+97.16	+97.52	0.36	2.02	0.39	1.31
May, 1948											
Fraser Brace extractor	100% V	0.8455	1.4733	1.4713	0.0020	+95.66	+98.10	2.44	1.45	1.50	3.99
Pipkin juice extractor	100% V	0.8431	1.4723	1.4710	0.0013	+96.66	+97.83	1.17	1.77	0.91	2.36
Screw press	100% V	0.8426	1.4721	1.4712	0.0009	+97.59	+98.32	0.73	1.38	0.95	2.11
Pipkin roll	100% V	0.8425	1.4719	1.4710	0.0009	+97.73	+98.19	0.46	1.72	1.01	1.57

* H = Hamlin, PB = Parson Brown, P = Pineapple, S = Seedling, V = Valencia.

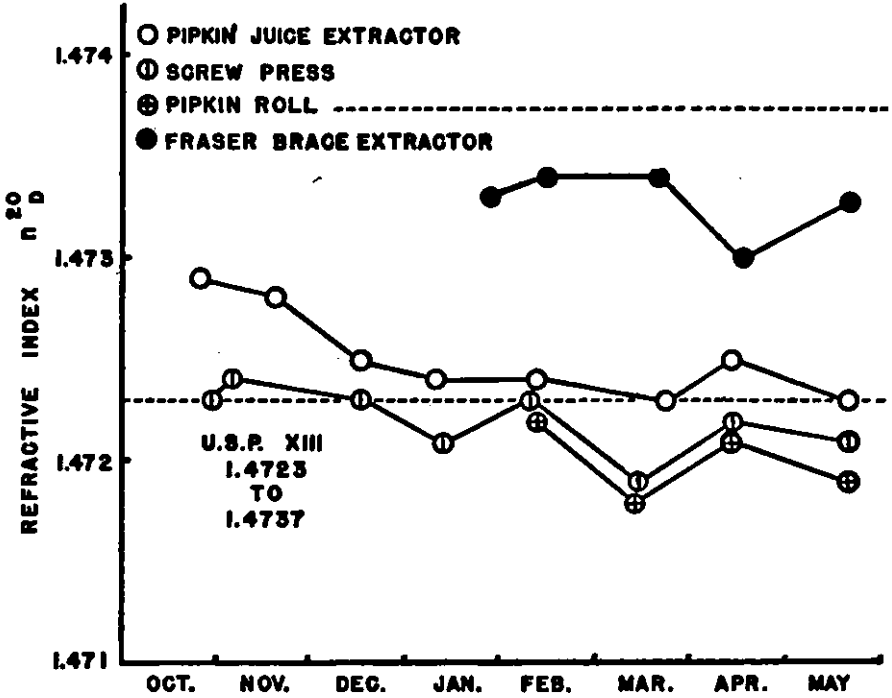


Fig. 11.—Refractive index of coldpressed orange oils extracted by four different methods during the 1947-48 season.

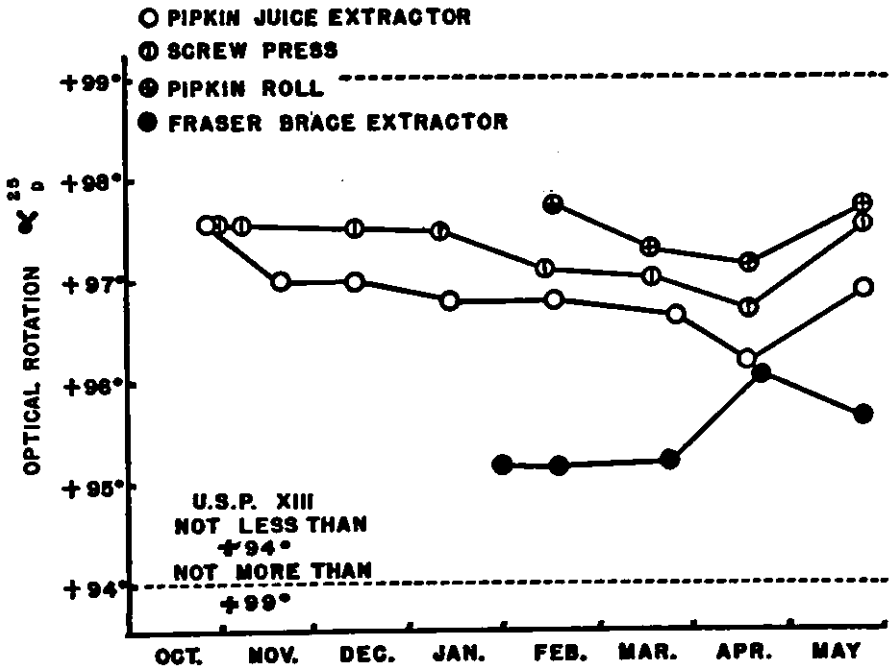


Fig. 12.—Optical rotation of coldpressed orange oils extracted by four different methods during the 1947-48 season.

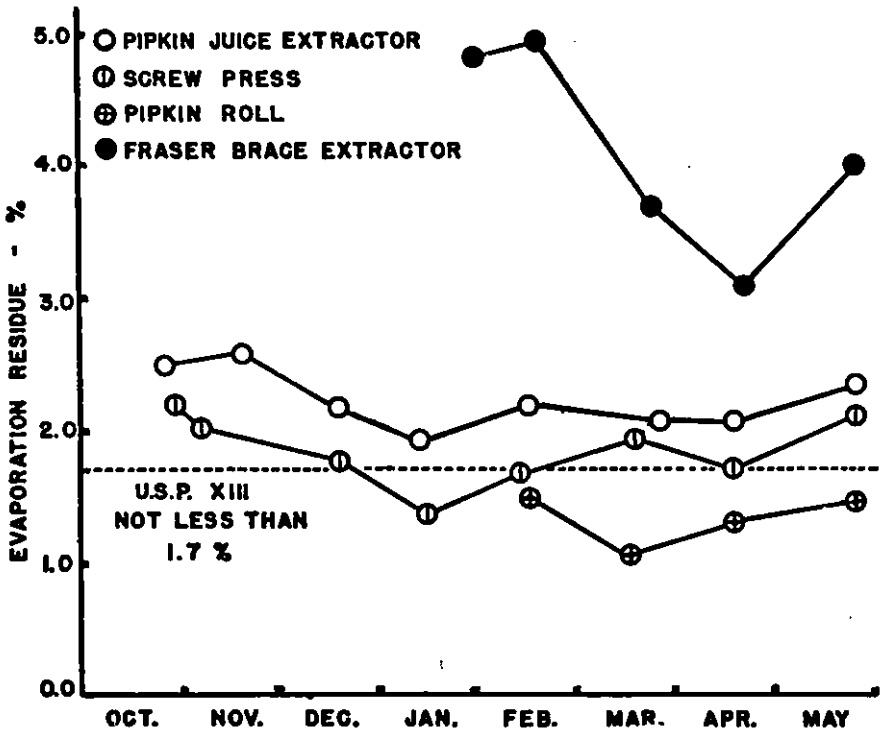


Fig. 13.—Evaporation residue of coldpressed orange oils extracted by four different methods during the 1947-48 season.

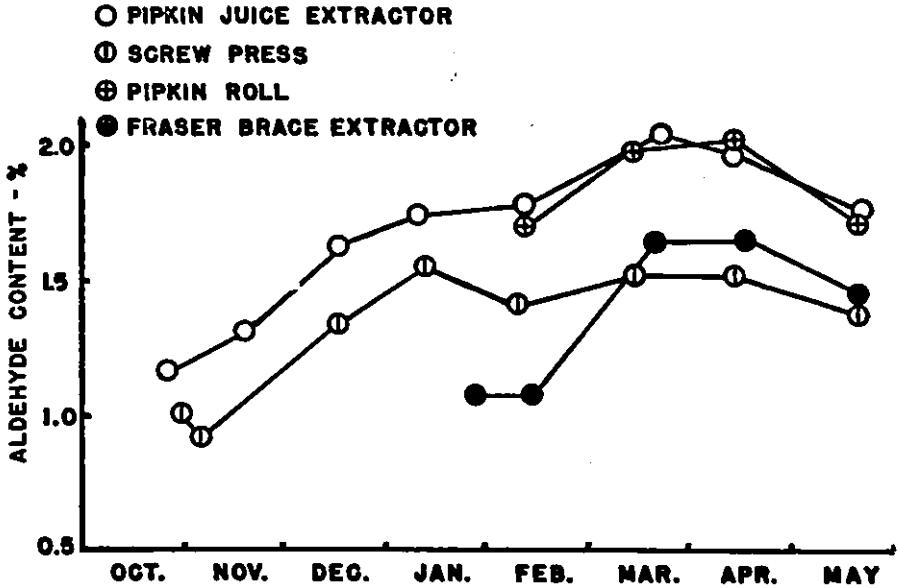


Fig. 14.—Aldehyde content of coldpressed orange oils extracted by four different methods during the 1947-48 season.

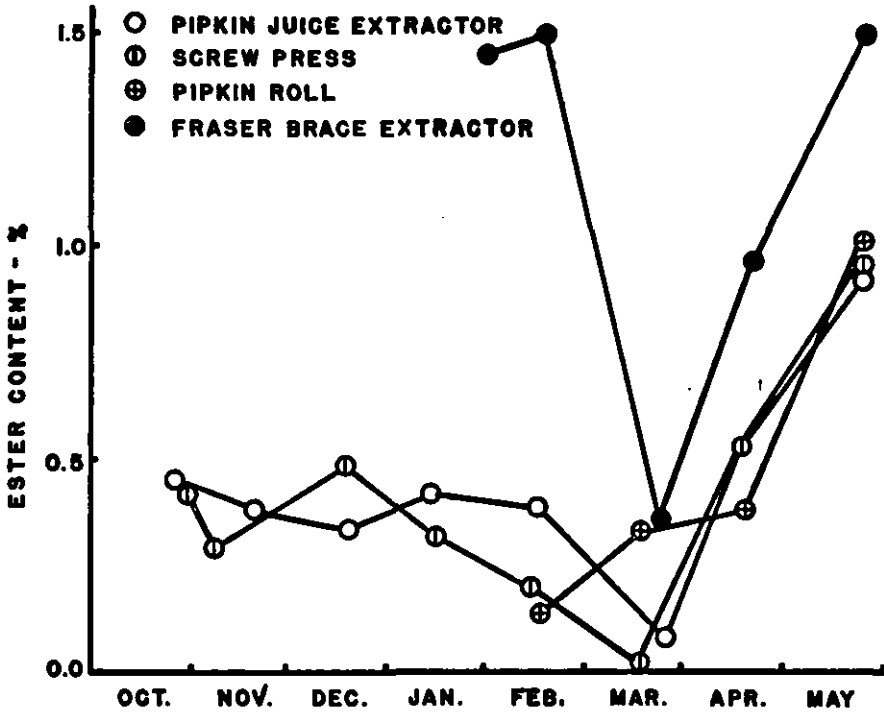


Fig. 15.—Ester content of coldpressed orange oils extracted by four different methods during the 1947-48 season.

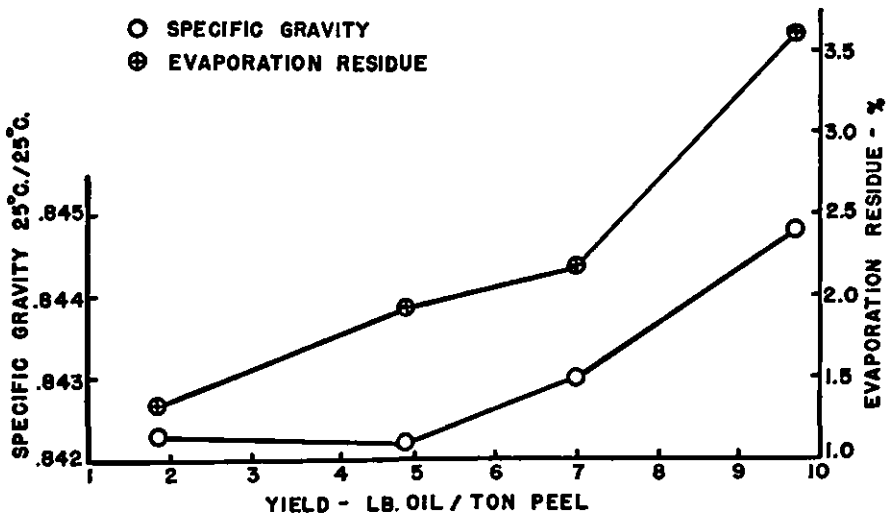


Fig. 16.—Relation of specific gravity and evaporation residue of coldpressed orange oils to yield.

Data secured at the various processing plants pertaining to the yields of oil obtained by the different methods of extraction

are presented in Table 3 and Figs. 2, 3, 5, and 7. Table 3 also shows the relationship between the yields of coldpressed orange oils, which were obtained by the four methods of extraction, and all of the physical and chemical properties of the oils, except the aldehyde content. Data for all four of the different methods of extraction are not available for the months prior to February; therefore, they could not be used to secure average values for comparison purposes. The data presented are average values for the three months, March, April, and May, and also were

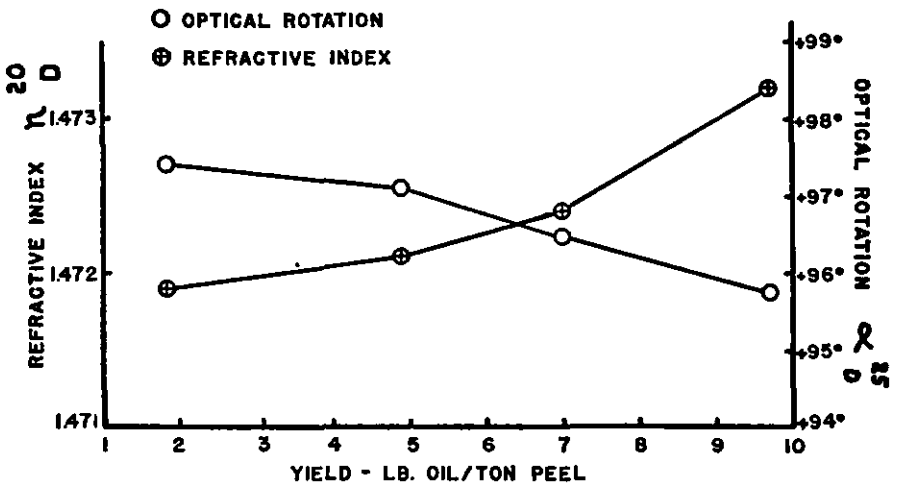


Fig. 17.—Relation of refractive index and optical rotation of coldpressed orange oils to yield.

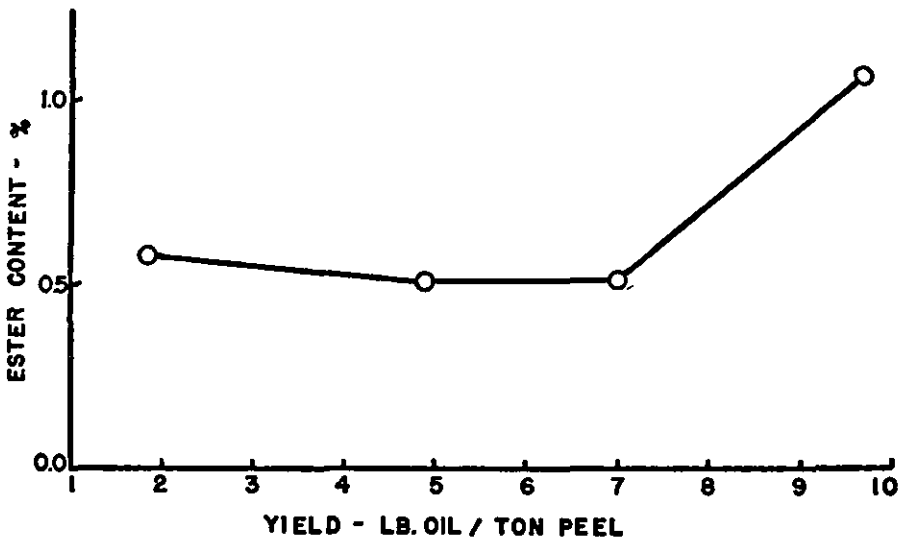


Fig. 18.—Relation of ester content of coldpressed orange oils to yield.

TABLE 3.—RELATION OF YIELD TO THE CHARACTERISTICS OF FLORIDIAN OIL OF ORANGE.

Yield Lb. Oil/Ton Peel	Specific Gravity 25° C./25° C.	Evaporation Residue Percent	Optical Rotation α 25 D	Refractive Index 20 n D	Ester Content Percent	Method of Extraction
9.70	.8448	3.60	+95.66	1.4732	0.94	Fraser Brace extractor
7.00	.8430	2.18	+96.49	1.4724	0.51	Pipkin juice extractor
4.90	.8422	1.92	+97.11	1.4721	0.51	Screw press
1.85	.8423	1.32	+97.41	1.4719	0.58	Pipkin roll

secured during those months when only one variety, Valencia, of oranges was being processed. Figures 16, 17, and 18 present these results in graphic form.

The relationship between the aldehyde content of expressed oil of orange and the quantity of aqueous phase, which comes in contact with the oil during processing, can be seen in Table 4 and Fig. 19. Here, also, the average values for the aldehyde content of samples of oil secured during March, April, and May are used. The results secured for oils which were extracted during January and February by the Fraser Brace extractor were not included in these average values because a basic change was

TABLE 4.—EFFECT OF QUANTITY OF AQUEOUS PHASE ON THE ALDEHYDE CONTENT OF FLORIDIAN OIL OF ORANGE.

Aqueous Phase Gal./Gal. Oil	Aldehyde Content %	Method of Extraction
12.5	1.93	Pipkin juice extractor
21.5	1.91	Pipkin roll
100.0	1.58	Fraser Brace extractor
190.0	1.47	Screw press

made in this processing method after these samples of oil had been obtained. Extremely large quantities of water were being used with this extractor during January and February. In March the amount of water used was reduced to give 100 gallons of an aqueous phase per gallon of oil produced and the oil extracted in that month contained 52 percent more aldehyde than the February sample.

The analyses of samples of expressed oil of orange, extracted during March, April, May, and June from Valencia oranges by the Pipkin juice extractor, are given in Tables 5 and 6. Values in Table 5 are for oil which was extracted from fruit on the day it was harvested; the data in Table 6 refer to oil extracted from fruit which was held in storage bins from three to five days prior to its extraction. The differences between the average values of the properties of the oils immediately extracted and the oils extracted from the stored fruit are presented in Table 7. Significant differences were found only in the chemical properties of these oils.

COLDPRESSED AND DISTILLED OILS OF ORANGE, GRAPEFRUIT, TANGERINE, AND LIME

Table 8 includes the maximum and minimum values of the physical and chemical characteristics of coldpressed and distilled

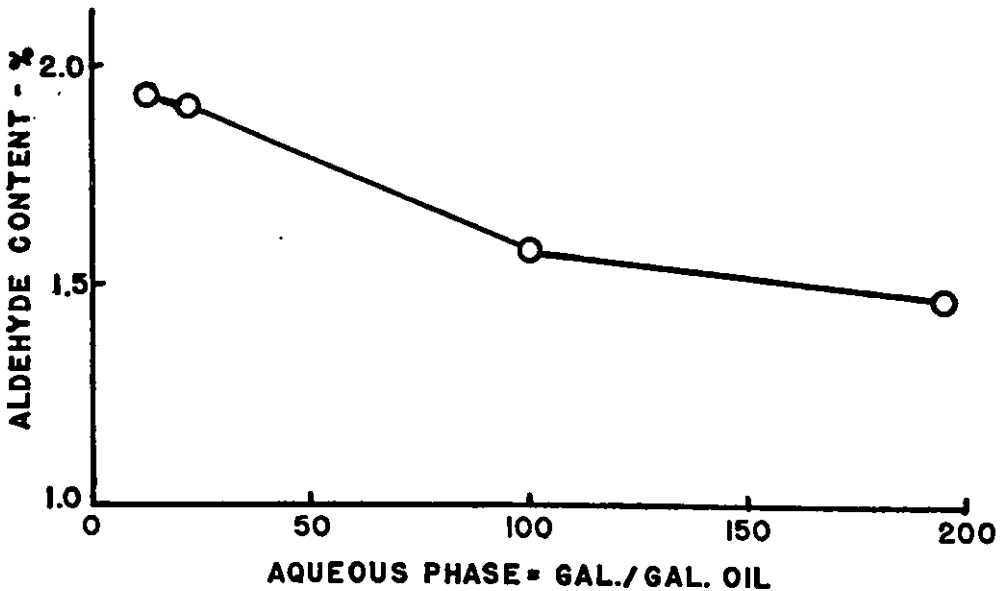


Fig. 19.—Influence of the quantity of aqueous phase which comes in contact with the oil during processing on the aldehyde content of coldpressed orange oils.

TABLE 5.—PROPERTIES OF OIL OF ORANGE EXPRESSED FROM FRUIT ON THE DAY HARVESTED.

Date	Quantity of Oil Sampled Lb.	Variety of Fruit	Specific Gravity 25°C./25°C.	Refractive Index n _D ²⁰	Refractive Index of 10% Distillate n _D ²⁰	Difference	Optical Rotation α _D ²⁵	Optical Rotation of 10% Distillate α _D ²⁵	Difference	Aldehyde Content %	Ester Content %	Evaporation Residue %
3-22-48	11,000*	Valencia	0.8428	1.4723	1.4708	.0015	+96.61	+96.96	0.35	2.04	0.08	2.08
4-8-48	11,000	Valencia	0.8427	1.4725	1.4714	.0011	+96.38	+97.44	1.06	1.94	0.53	2.07
4-14-48	11,000	Valencia	0.8431	1.4725	1.4712	.0013	+96.19	+97.21	1.02	1.97	0.53	2.09
5-10-48	11,000	Valencia	0.8427	1.4722	1.4712	.0010	+97.26	+97.76	0.50	1.84	0.71	1.85
6-1-48	11,000	Valencia	0.8428	1.4719	1.4707	.0012	+97.29	+97.77	0.48	1.65	0.60	1.98
6-21-48	11,000	Valencia	0.8427	1.4719	1.4709	.0010	+96.97	+98.37	1.40	1.45	0.45	1.74
		Average	0.8428	1.4722	1.4710	.0012	+96.78	+97.58	0.80	1.82	0.48	1.97

* Each 11,000 pounds of oil represents approximately 70,000 boxes of fruit.

TABLE 6.—PROPERTIES OF OIL OF ORANGE EXPRESSED FROM FRUIT STORED IN FRUIT BINS FOR THREE TO FIVE DAYS.

Date	Quantity of Oil Sampled Lb.	Variety of Fruit	Specific Gravity 25°C./25°C.	Refractive Index n_D^{20}	Refractive Index of 10% Distillate n_D^{20}	Difference	Optical Rotation α_D^{25}	Optical Rotation of 10% Distillate α_D^{25}	Difference	Aldehyde Content %	Ester Content %	Evaporation Residue %
3-19-48	11,000*	Valencia	0.8430	1.4723	1.4708	.0015	+96.61	+96.96	0.35	1.92	0.25	2.07
4-10-48	11,000	Valencia	0.8426	1.4725	1.4710	.0015	+96.39	+97.23	0.84	1.89	0.60	2.17
4-14-48	11,000	Valencia	0.8432	1.4723	1.4709	.0014	+96.52	+97.20	0.68	1.89	0.63	2.33
5-10-48	11,000	Valencia	0.8421	1.4722	1.4711	.0011	+96.78	+97.50	0.72	1.76	0.86	2.18
6-1-48	11,000	Valencia	0.8428	1.4720	1.4709	.0011	+96.89	+98.17	1.28	1.59	0.77	2.14
6-21-48	11,000	Valencia	0.8426	1.4719	1.4708	.0011	+97.29	+98.37	1.08	1.40	0.68	2.09
		Average	0.8427	1.4722	1.4709	.0013	+96.74	+97.57	0.83	1.74	0.63	2.16

* Each 11,000 pounds of oil represents approximately 70,000 boxes of fruit.

TABLE 7.—INFLUENCE OF STORAGE OF FRUIT, PRIOR TO EXTRACTION, ON THE PROPERTIES OF COLDPRESSED OIL OF ORANGE.

	Oil Expressed from Fruit Soon After Harvesting (Table 5)	Oil Expressed from Fruit After Storage (Table 6)	Difference	% Difference
Specific gravity 25°C./25°C.	0.8428	0.8427	0.0001	Not significant
Refractive index n_D^{20}	1.4722	1.4722	0.0000	Not significant
Refractive index 10% distillate n_D^{20}	1.4710	1.4709	0.0001	Not significant
Difference	0.0012	0.0013	0.0001	Not significant
Optical rotation α_D^{25}	+96.78	+96.74	0.04	Not significant
Optical rotation 10% distillate α_D^{25}	+97.58	+97.57	0.01	Not significant
Difference	0.80	0.83	0.03	Not significant
Aldehyde content %	1.82	1.74	0.08	4.6
Ester content %	0.48	0.63	0.15	31.3
Evaporation residue %	1.97	2.16	0.19	9.6

orange oils that were secured during the 1947-48 season. Similar data for expressed and distilled grapefruit and tangerine oils are given in Table 9, which also includes results obtained from the analyses of 10 samples of stripper oils from citrus molasses plants.

The maximum and minimum values for the properties of expressed and steam distilled Persian lime oil are listed in Table 10. Also included in this table are results from the analysis of one sample of steam distilled oil from Meyer lemon. Properties of Meyer lemon oil indicate that it is predominantly lemon in character, although the Meyer lemon is commonly believed to be a natural hybrid.

DISCUSSION OF RESULTS

RELATION OF YIELD TO PROPERTIES AND U. S. P. SPECIFICATIONS

The factor found to influence the physical and chemical properties of coldpressed oil of orange to the greatest extent was the yield of oil secured from the peel. As shown in Table 3 and Figs. 16 and 17, as the yield increased the values of the specific gravity, evaporation residue, and refractive index also increased, but the values of the optical rotation decreased. Thus the percentage of the total amount of oil in the peel that is extracted determines the characteristics of the oil and, therefore, its final quality. As the yield of oil is increased, more high-boiling, high-molecular weight constituents are evidently extracted, and the presence of a greater percentage of these compounds in the oil causes a reduction in the percentage of d-limonene, resulting in lower optical rotation values, since d-limonene is the most optically active component in the oil.

The yield of oil obtained by the various methods of processing varied from 1.85 lbs./ton peel to 9.70 lbs./ton peel. Commercial plants often have more peel than it is possible for them to process and still obtain the maximum amount of oil recoverable from the peel. This being the case, the plants are operated in such a manner as to produce the maximum amount of oil on an hourly basis. To do this they partially extract the oil from a large quantity of peel rather than secure the maximum recovery of oil from a smaller quantity of peel. By operating in this manner they may secure very low yields of oil, despite the fact that they are capable of obtaining much higher yields with the use of the same equipment. The yields of oil secured using the Pipkin

TABLE 8.—MAXIMUM AND MINIMUM VALUES FOR THE PHYSICAL AND CHEMICAL PROPERTIES OF ORANGE OILS PRODUCED IN FLORIDA DURING 1947-48 SEASON.

Type of Oil	Coldpressed										Vacumm Steam Distilled	
Method of Extraction	All Methods		Pipkin Roll		Screw Press		Fraser Brace Extractor		Pipkin Juice Extractor		De-Oiler Oil	
Number of samples analyzed	35		4		8		6		17		9	
	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum
Specific gravity 25°C./25°C.	0.8458	0.8416	0.8425	0.8420	0.8426	0.8416	0.8458	0.8441	0.8433	0.8420	0.8464	0.8400
Refractive index n_D^{20}	1.4734	1.4718	1.4722	1.4718	1.4724	1.4719	1.4734	1.4730	1.4729	1.4722	1.4732	1.4715
Refractive index of 10% distillate n_D^{20}	1.4715	1.4703	1.4711	1.4708	1.4712	1.4707	1.4713	1.4703	1.4715	1.4707
Difference	0.0031	0.0008	0.0013	0.0009	0.0015	0.0008	0.0031	0.0017	0.0015	0.0010
Optical rotation α_D^{25}	+97.76	+95.16	+97.76	+97.16	+97.59	+96.69	+96.30	+95.16	+97.57	+96.19	+98.56	+95.92
Optical rotation of 10% distillate α_D^{25}	+98.70	+96.81	+98.19	+97.52	+98.32	+97.24	+98.70	+96.96	+97.89	+96.81
Difference	2.44	0.00	0.85	0.01	0.73	0.03	2.44	1.51	1.30	0.00
Aldehyde content %	2.04	0.92	2.02	1.70	1.55	0.92	1.65	1.08	2.04	1.17	2.48	1.72
Ester content %	1.63	0.04	1.01	0.15	0.95	0.04	1.63	0.35	1.09	0.08	1.38	0.22
Evaporation residue %	4.93	1.07	1.57	1.07	2.20	1.38	4.93	3.12	2.59	1.85	1.24	0.08

TABLE 9.—MAXIMUM AND MINIMUM VALUES FOR THE PHYSICAL AND CHEMICAL PROPERTIES OF SOME CITRUS OILS PRODUCED IN FLORIDA DURING 1947-48 SEASON.

Type of Oil	Grapefruit				Tangerine		Stripper Oil**	
	6		9		1	1	10	
	Coldpressed		Distilled*		Cold-pressed	Dis-tilled	Distilled	
	Maximum	Minimum	Maximum	Minimum			Maximum	Minimum
Number of samples analyzed								
Specific gravity 25°C./25°C.	0.8532	0.8508	0.8539	0.8415	0.8456	0.8407	0.8443	0.8398
Refractive index n_D^{20}	1.4761	1.4746	1.4746	1.4714	1.4734	1.4720	1.4721	1.4713
Refractive index of 10% distillate n_D^{20}	1.4712	1.4698	1.4711
Difference	0.0054	0.0038	0.0023
Optical rotation α_D^{25}	+92.96	+91.19	+96.50	+91.50	+91.18	+93.67	+98.90	+95.55
Optical rotation of 10% distillate α_D^{25}	+98.14	+95.81	+92.68
Difference	6.33	3.68	1.50
Aldehyde content %	1.67	1.49	4.06	2.30	1.08	1.24	1.50	0.47
Ester content %	4.20	2.11	2.52	0.08	0.34	0.25	2.46	0.07
Evaporation residue %	8.02	6.02	3.66	0.19	4.53	0.20	0.79	0.03

* Vacuum steam distilled (de-oiler oil).

** By-product from manufacture of citrus molasses.

TABLE 10.—CHARACTERISTICS OF ESSENTIAL OILS SECURED FROM PERSIAN LIME AND MEYER LEMON.

Type of Oil	Persian Lime				Meyer Lemon
	6		5		1
	Coldpressed		Steam Distilled		Steam Distilled
	Maximum	Minimum	Maximum	Minimum	
Specific gravity 20°C./20°C.	0.8823	0.8798	0.8579	0.8556	0.8555
Refractive index n_D^{20}	1.4853	1.4842	1.4751	1.4743	1.4740
Refractive index of 10% distillate n_D^{20}	1.4731	1.4729
Difference	0.0123	0.0112
Optical rotation α_D^{20}	+41.80	+38.60	+50.52	+46.84	+56.00
Optical rotation of 10% distillate α_D^{20}	+49.24	+47.60
Difference	9.88	7.00
Aldehyde content %	5.52	3.66	2.71	1.61	1.19
Ester content %	8.20	7.42	3.49	2.41	2.45
Evaporation residue %	14.67	12.95	1.23	0.18	0.16

roll and screw press methods of extraction, as shown in Table 3, appear to be low when compared to the yields obtained by the other methods of extraction, but this is caused by the operation of the equipment from an efficiency standpoint on an hourly rather than a yield basis. Quality of the oil depends upon its properties, which are influenced by the yield obtained, which in turn is determined by operational procedure of the equipment used and other processing techniques.

Analyses of expressed oils of orange secured during the 1947-48 season indicate that the oil produced by some of the manufacturing processes at certain times during the season did not meet the U. S. P. (24) specifications, because some of the processes resulted in yields which were too low or too high. Only one method of extraction gave yields throughout the season so that the oil consistently met the requirements of the U. S. P. However, it is apparent that if oil is extracted in such manner that the yield falls within a certain range, then it will meet U. S. P. specifications.

Utilization of data obtained during this investigation will make it possible for any processor to produce an oil which will meet U. S. P. specifications, provided he is willing to change his manufacturing procedures. He may still use available equipment in such manner that he will secure a yield of oil having these properties which are indicative of good quality. Excessively high or low yields should be decreased or increased by the mode of operation of the extraction equipment. Based upon the data accumulated during the past year, it is estimated that a yield of 6.5 to 8.5 pounds of oil per ton of peel from mid-season oranges or the extraction of 45 to 60 percent of the total amount of oil in the peel of any variety of fruit of good maturity will result in a coldpressed oil of orange that will meet the specifications of the United States Pharmacopoeia (24). It might also be added that oil extracted about the middle of May from Valencia oranges which had passed peak maturity did not meet U. S. P. standards. The reason that this late-season oil was of lower quality was that low yields of oil were obtained with this type of fruit because the peel had become soft and pliable, making the extraction of the oil more difficult.

EFFECT OF AQUEOUS PHASE ON ALDEHYDE CONTENT

The flavor quality of oil of orange is dependent upon the many constituents of which it is composed. The aldehyde content of the oil, although not included in the U. S. P. specifications, is

indicative of the flavoring qualities of the oil. Although other constituents are also very important from a flavor standpoint, aldehydes are a predominant factor in orange and other citrus oils. The data in Table 4 and Fig. 19 indicate that the aldehyde content decreases as the amount of aqueous phase which comes in contact with the oil during processing is increased. The average aldehyde content of the expressed oils of orange, secured during March, April, and May from the four plants at which material balance studies were made, varied from 1.47 to 1.93 percent. In one plant, where, at the suggestion of the authors, the water used in the process was reduced from extremely large quantities to an amount sufficient to give 100 gallons of aqueous phase per gallon of oil produced, while other variable factors were kept constant, the aldehyde content increased from 1.08 to 1.64 percent, or 52 percent. Thus, it is evident that to produce an orange oil of high aldehyde content, the amount of aqueous phase allowed to come in contact with the oil during processing should be reduced to as small a quantity as is practically possible under operating conditions.

RELATION OF FRUIT VARIETY TO PROPERTIES

Consideration of Table 2 and Figs. 10, 11, and 12 shows that the oils manufactured by any one process fell within a particular category of their own and remained there throughout the season. The differences in the physical properties of expressed orange oils that were obtained from different varieties of fruit by any particular process were not significant, except in the case of the Fraser Brace method of extraction where, during the month of April, an apparently erratic variation occurred.

The aldehyde content of coldpressed oils of orange, as can be seen from Table 2 and Fig. 14, was highest when made from Valencia oranges. Mixtures of Pineapple and seedling oranges gave an oil with a lower aldehyde content, and mixtures of Hamlin and Parson Brown varieties yielded the lowest aldehyde content oil.

The variety of the fruit apparently had very little effect on the ester content of the orange oils. Oil of orange produced by the Fraser Brace extractor from mid-season varieties that were partially green in color was considerably higher in ester content than that made by the same process later in the season from the same varieties when they were completely orange in color, and it was also higher in esters than oils produced by the other

methods. High evaporation residue values also were found for the oils produced by the Fraser Brace extractor.

STORAGE OF FRUIT PRIOR TO OIL EXTRACTION

Results obtained indicate that the length of time fruit was stored prior to the extraction of the oil was another factor which influenced the characteristics and quality of the oil. This is illustrated by the data presented in Tables 5, 6, and 7, which show the effect storage of the fruit had upon the physical and chemical properties of the oil. There were no significant differences in the physical properties of coldpressed oils of orange extracted from fruit on the same day it was harvested and those extracted from fruit having been stored in fruit bins for three to five days before the oils were extracted. However, significant differences were found in the chemical properties. The ester content of the oil secured from stored fruit was 31.3 percent higher than that extracted from fruit which had not been stored. The evaporation residue of the oil from the stored fruit was 9.6 percent greater and the aldehyde content was 4.6 percent smaller than these properties of the oil from the fruit which was not stored.

EFFECT OF MATURITY ON PROPERTIES

In the studies of the effect of fruit storage on oil quality, all samples of the oil of orange were extracted by the same process and secured from the same variety of fruit. Therefore, over a period of four months information was obtained in reference to the effect of maturity on the properties of the oil. Here, again, differences were noted in the chemical characteristics rather than in the physical properties. The aldehyde content of Valencia orange oils increased as maturity increased, reached a maximum when extracted during the early part of the Valencia season from fruit that just passed the maturity standards, and then decreased after peak maturity had been reached. The ester content of these oils was lowest when extracted during the early part of the Valencia season and gradually increased as the fruit became more mature. Valencia oranges that had passed peak maturity produced an oil with the highest ester content of any oils secured during the year.

COMPARISON OF COLDPRESSED AND DISTILLED OILS

Comparison in Table 8 of the analyses of coldpressed oils of orange with those of vacuum steam distilled oils of orange,

which were secured from the cannery deoilers, showed that the distilled oils had an aldehyde content 24 percent higher and an ester content 10 percent lower than the corresponding values for coldpressed oils. Similarly, as seen in Table 9, distilled oil of grapefruit was 90 percent higher in aldehydes and 60 percent lower in esters than the expressed oil. From these results it was evident that large quantities of aldehydes were removed from the citrus juice itself by the deoilers during commercial canning operations. Also it is indicated that the removal of oil from the juice by the deoilers results in the fractionation of the peel oil originally present, so that the small quantity of oil which remains in the canned juice will have different characteristics from either expressed or distilled oils.

A comparison of the properties of stripper oils that were obtained from the press liquor in citrus molasses plants with the properties of other types of oils cannot be made because the press liquor was often obtained from a mixture of orange and grapefruit peel.

COMPARISON OF FLORIDIAN ESSENTIAL OILS WITH OILS FROM OTHER SOURCES

Data presented in Tables 11 and 12 show how various types of Floridian essential oils compare with similar types of oils from California and various foreign countries. All of the data in these tables for Floridian oils are based on results secured during this investigation. The data for the oils from other sources are those given by Guenther (7), (8), (9), (10) and are based upon the analysis of many samples of these oils in the laboratories of Fritzsche Brothers, Inc., New York. From the comparison of the properties presented in these tables it is evident that Florida citrus oils can be equal or superior to essential oils from any other source. Further research is being undertaken in reference to the flavoring qualities of the essential oils produced in Florida in order to demonstrate that they can consistently be manufactured with high flavoring quality.

SUMMARY

Commercial methods of production of essential oils in Florida during the 1947-48 season have been studied and compared.

The physical and chemical properties of 83 samples of coldpressed and distilled oils of orange, grapefruit, tangerine, and lime have been determined. Properties of Meyer lemon oil and

TABLE 11.—COMPARISON OF FLORIDIAN COLDPRESSED ORANGE OIL WITH OILS FROM OTHER SOURCES.

	U.S.P. XIII Specifications Coldpressed Orange	Floridian Coldpressed Orange			Californian Coldpressed Orange		Italian Coldpressed Orange		Guinea Coldpressed Orange		Brazilian Coldpressed Orange	
		Maxi- mum	Mini- mum	Average	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum
Specific gravity (25° C./25° C.)	0.842 to 0.846	0.846	0.842	0.843	0.846	0.843	0.846	0.843	0.845	0.840	0.847	0.842
Refractive index (20° C.)	1.4723 to 1.4737	1.4734	1.4718	1.4724	1.4742	1.4731	1.4740	1.4729	1.4742	1.4721	1.4747	1.4723
Evaporation residue %	not less than 1.7%	4.9	1.1	2.2	5.1	3.5	4.3	1.4	2.4	1.1	4.8	2.2
Optical rotation (25° C.)	not less than +94° and not more than +99° in 100mm tube	+97.76°	+95.16°	+96.75°	+98.33°	+94°	+97.17°	+95.5°	+98°	+94°	+97.87°	+95.0°

TABLE 12.—COMPARISON OF FLORIDIAN ORANGE AND LIME OILS WITH OILS FROM OTHER SOURCES.

	Distilled Orange					Coldpressed Lime					Distilled Lime				
	Floridian			Californian		Floridian			West Indian and Mexican		Floridian			West Indian and Mexican	
	Maximum	Minimum	Average	Maximum	Minimum	Maximum	Minimum	Average	Maximum	Minimum	Maximum	Minimum	Average	Maximum	Minimum
Specific gravity (25°C./25°C.)	0.846	0.840	0.842	0.842	0.840	0.882 (20°C.)	0.880 (20°C.)	0.881 (20°C.)	0.886 (15°C.)	0.878 (15°C.)	0.858 (20°C.)	0.856 (20°C.)	0.857 (20°C.)	0.868 (15°C.)	0.862 (15°C.)
Refractive index (20°C.)	1.4732	1.4715	1.4720	1.4730	1.4717	1.4853	1.4842	1.4849	1.4860	1.4800	1.4751	1.4743	1.4747	1.4770	1.4750
Evaporation residue %	1.24	0.08	0.47	1.0	0.5	14.67	12.95	13.74	13.5	10	1.23	0.18	0.60		
Optical rotation	+98.56° (25°C.)	+95.92° (25°C.)	+97.62° (25°C.)	+99.1° (25°C.)	+98° (25°C.)	+41.80° (20°C.)	+38.60° (20°C.)	+40.55° (20°C.)	+40°	+35°	+50.52° (20°C.)	+46.84° (20°C.)	+48.02° (20°C.)	+46°	+35°
Aldehyde content—% (as citral)	2.48*	1.72*	1.99*			5.52	3.66	4.92	8.5	4.5	2.71	1.61	2.03	1.5	0.5

* As decyl aldehyde.

stripper oils also are reported. Coldpressed and distilled oils of orange and grapefruit were found to have very large differences in their aldehyde and ester contents.

Fruit variety, degree of maturity, and storage of fruit before extraction were found to be factors which affected significantly the chemical properties of expressed oil of orange. These factors did not affect to any extent the physical characteristics of the oil.

Quality of citrus peel oils, as indicated by their physical and chemical characteristics, is determined by the yield of oil obtained in any commercial process, regardless of the type of extraction equipment used, and also by the quantity of aqueous phase that comes in contact with the oil during processing, since the aldehyde content of the oil is largely determined by this factor.

The use of proper processing methods results in the production of essential oils in Florida which are of the highest quality and which consistently meet the specifications of the United States Pharmacopoeia. When manufactured carefully, Florida citrus oils are equal or superior in quality to essential oils from any other sources.

ACKNOWLEDGMENTS

Acknowledgments are made to the commercial processors and manufacturers in the State of Florida whose earnest cooperation contributed much to the success of this work. Coldpressed oil samples used in this study were obtained from Essential Oil Producers, Inc., Dunedin; Pasco Packing Company, Dade City; Florida Citrus Oil Company, Lake Alfred; and Fraser Brace Engineering Company, Tampa. The distilled oils were secured from Florida Citrus Cannery Cooperative, Lake Wales; Wm. P. McDonald Corporation, Auburndale; Floridagold Citrus Corporation, Lake Alfred; Dr. P. Phillips Canning Company, Orlando; and Essential Oil Producers, Inc., Dunedin. The stripper oils were furnished by the Florida Molasses Corporation, Lake Alfred; Adams Packing Association, Auburndale; Citrus Cannery Cooperative, Lake Wales; and Pasco Packing Company, Dade City. The authors are indebted to Dr. F. W. Wenzel for his contribution to the organizing and editing of this bulletin. Acknowledgment is made to V. H. Ragsdale and E. C. Parrish for their assistance in securing part of the analytical data. For all of these courtesies and contributions the authors express their appreciation and thanks.

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