in meal as low as 0.006% to release enough solvent to attain the lower explosive limit in any ordinary confined storage space. This would be due mainly to the "holding power" of the 1% oil content almost certain to be present. The failure to obtain flashes at the lower solvent percentages is probably due in part to absorption of hexane in the oil content of the meal.

This method is believed to provide test conditions considerably more severe than those likely to be attained in commercial operations.

The apparatus required is simple, and it should be possible to fabricate it in most small machine shops. The method is not elaborate and with careful operation should yield reliable and duplicable results. The preliminary results indicate that it may be sufficiently sensitive.

Recommendations

It is recommended that this method be tried by other members of the subcommittee and by any others in the industry who are interested. The results obtained should then be subject to rigorous analysis to determine whether the method has sufficient merit to be considered for plant control purposes.

A drawing of the concentric ring copper cup tester will be made available on request to those interested in constructing a cup for experimental or control purposes.

Summary

The hazards of excess residual solvent in solvent-extracted meals and methods currently used for its measurement are discussed. Preliminary results are reported with a simple copper-cup flash-tester with concentric rings as heating surfaces. Solvent contents as low as 0.03% can be detected. The method is semi-quantitative. The method may be useful for plant control purposes.

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[Received October 23, 1959]

Continuous Refining of Crude Coconut Oil in a Pressure System[1]

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REFINING of crude vegetable oils has progressed from the art of kettle refining as practiced 25 years ago to the science of modern continuous centrifugal processing. This statement is commonly accepted for such oils as soybean, cottonseed, peanut, and corn. However when we discuss the short-chain lauric acid oils (1) such as coconut, babassu, and palm kernel, we find the general practice is still to use the antiquated kettle method.

A study of these lauric acid oils indicates that they are readily saponified when processed in the earlier type of standard continuous caustic soda process with its comparatively long mixing contact time of oil with lye. The high excess of caustic soda over the stoichiometric amounts, as used in conventional refining, leads to large amounts of saponification. These factors in the phase system oil-soap-water, and oftentimes the added factor of entrained air when using open discharge centrifugals, tend to form stable emulsions which defy efficient separation even under the high gravitational field of centrifugal force.

With the development of the all-Hermetic continuous refining process (2, 3) the problem of air entrainment during separation was eliminated. After much intensive research the other factors, such as reagent concentration, temperature, and mixing, were determined and now may be specifically controlled to give a high quality of refined oil and at the same time a high refining yield.

Theoretical Background

After considerable study of the basic problem the McBain (4, 5) phase diagrams for aqueous soap systems were selected as a starting point. For purposes of illustration, Figure 1 shows in part the phase behavior of sodium laurate, electrolyte, and water at 90°C. (6). This system with weight percentage of anhydrous soap (sodium laurate) as the ordinate and weight percentage of electrolyte as the abscissa is divided into various phase areas.

For background information the diagram will first be described before showing its relationship to the

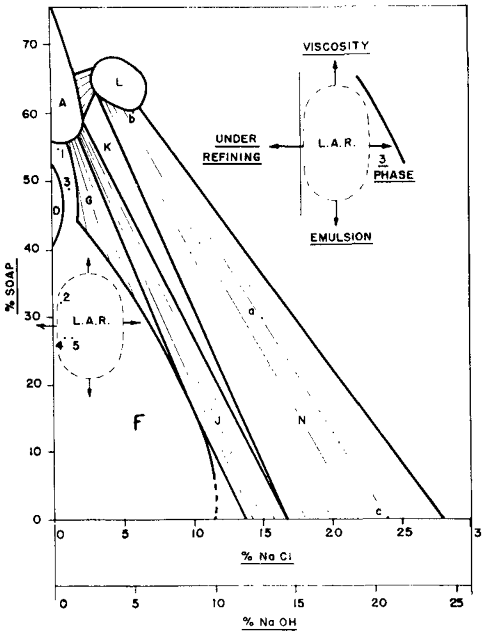

FIG. 1. Sodium laurate at 90°C.

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[1] Presented at the 33rd Annual Fall Meeting, American Oil Chemists' Society, Los Angeles, Calif., September 28–30, 1959.

TABLE I

Coconut Oil Refining Data

Sample	No.	% FFA		% NaOH d.b. added[a]	Soapstock				Refining loss	Refining factor[d]		Comments
		Lauric	Oleic		% Soap	% NaOH	Viscosity c.p.	Phase[b] Area		As lauric	As oleic	
Oil I	1	3.2	4.5	0.67	55.2	0.5	68,000	D[c]	6.6	2.1	1.5	27°Bé lye
Oil I	2	3.2	4.5	0.67	32.0	0.3	43	F	4.6	1.4	1.0	Dilute 27°Bé to 13°Bé
Oil II	3	2.5	3.5	0.56	49.0	1.3	22,000	D[c]	5.1	2.1	1.5	24°Bé lye
Oil II	4	2.5	3.5	0.56	27.0	0.7	39	F	3.6	1.4	1.0	Dilute 24°Bé to 12°Bé
Oil III	5	1.7	2.4	0.42	27.0	1.0	50	F	2.4	1.4	1.0	12°Bé lye

[a] %NaOH (d.b.) on weight of crude oil.
[b] Phase on McBain diagram.
[c] Mixture neat and middle soap, area between D and G.
[d] Refining factor $= \frac{\%\ \text{Plant loss}}{\%\ \text{FFA}}$

refining of vegetable oils. In this particular diagram there are four angle-phase regions: A, D, F, and L, indicating homogeneous soap phase.

Area A is the neat soap phase existing only in the region between 56% and 76% soap at a 0% electrolyte content and decreasing in area up to a 2% electrolyte content. Neat soap is an anisotropic flowing crystalline material.

Area D indicates a middle soap. This is also anisotropic, differing from neat soap in that it has an extremely high viscosity. This abnormal viscosity causes it to act like a rubbery mass completely lacking in fluidity.

Area F is the isotropic nigre phase. It is extremely fluid and is usually dark in color on account of its tendency to dissolve impurities from the fat.

Area L is a kettle-wax which is a so-called "island" phase, containing a high soap and electrolyte content. This phase has a much greater viscosity than neat soap, hence is less fluid.

Certain other areas on the diagram consist of two phases and are shown with tie-lines, as for example Area N. These areas show regions of heterogeneous conditions which contain two components. When the composition of the system is brought into Area N, for example at point a, it would consist of 30% soap, 17% sodium hydroxide, and 53% water, which separates at 90°C. into kettle-wax (point b), containing 60% soap, 6.5% NaOH, and 33.5% water, and a free lye (point c), containing 0.1% soap, 27% NaOH, and 72.9% water. This would be considered a typical salting-out area.

There are also certain three-phase areas occurring, in which the composition of the three separating components is the same throughout the entire region. One such area is illustrated on the diagram as K (7).

Relationship of Phase Diagrams to Refining

With the soap phase diagrams as a theoretical basis, detailed and time consuming laboratory research was performed in order to correlate reaction time, reagent concentration, temperature, and mixing. From this study several basic rules were formulated for the refining of coconut oil. Simply stated, these are as follows:

a) The optimum refining yield was obtained when the soap was formed in the nigre phase (Area F) specifically bounded in the zone indicated as L.A.R.

b) The middle soap phase, Area D, must be avoided because of the high viscosity of the soap formed, which would hinder centrifugal separation.

c) Soaps formed in the Area A, neat soap, and in the Area L, kettlewax, are not desirable. These soaps do not readily dissolve color bodies and other impurities from the oil.

d) Large excess amounts of lye, or lye and salt, must be avoided otherwise the soap would be formed in the two-phase Areas J and N. In addition to undesirable excessive saponification of neutral oil, a salting-out effect would occur and form a three-phase condition in the centrifugal separator.

These few rules formulated for this study indicate the importance of forming the proper type of soap during the reaction of the reagent with the free fatty acids of the crude oil.

Commercial Processing

Following the experiences gathered from the laboratory work, pilot-plant trials, followed by full-scale commercial units for refining crude coconut oil, were placed in operation.

Table I illustrates typical data, condensed for ease of study, which was obtained from the refining of coconut oils on a commercial scale. Oils I and II, shown as Samples Number 1 through 4, indicate the great increase in refining yield possible when the soap is formed in the correct phase area. In both cases the refining yield was increased approximately 30% when the electrolyte concentration in the soapstock was regulated, allowing the soap to form in the specified nigre phase. Sample Number 5 is another typical refining result, indicating the high yield when coconut oil is processed under the properly controlled conditions. In all cases, as shown by the typical illustrations, the refining loss has been equal to the free fatty acid content calculated as oleic, or as a refining factor of 1.0, when treated under correct conditions. It should be mentioned at this point that, although lauric acid more closely corresponds to the average molecular weight of the acids present in coconut oil triglycerides, common practice in this country is to calculate the FFA as oleic acid as a basis for loss determinations. It is for this reason that the refining factor has been calculated for both lauric and oleic acid.

As may be seen from a study of the phase diagram, Figure 1, and the processing data, Table I, viscosity of the soap phase has an extremely important function in obtaining high-yield refining. The viscosity phenomenon was discussed in a previous paper describing its relationship to the soap phases in the manufacture of commercial soap (8).

With these data as shown in Figure 1 and Table I, a new zone has been added to the phase diagram, the so-called "lauric acid refining zone," and indicated as L.A.R. on the diagram in phase Area F. An enlarged schematic sectional view of this diagram is shown in the upper right-hand portion of Figure 1. Although the limits of this zone have not been completely defined, it may generally be stated that moving outside of this zone will result in the following: a) decreasing the soap concentration, at a constant electrolyte content, tends to form emulsion; b) in-

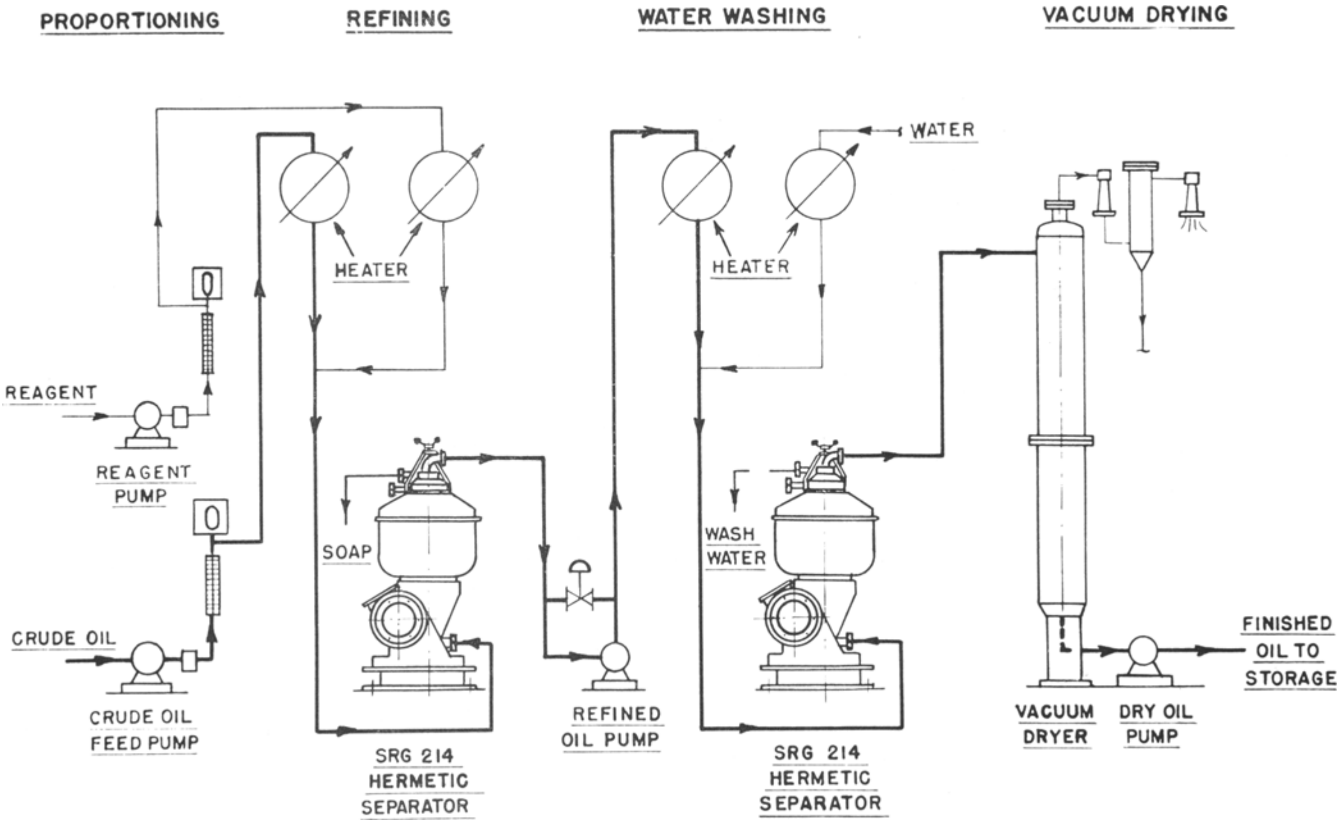

FIG. 2. Flow sheet for continuous coconut oil refining process.

creasing the soap concentration, at a constant electrolyte content, tends to move the system into a high viscosity area; c) decreasing the electrolyte content, at a constant soap concentration, will produce underrefining of the oil; and d) increasing the electrolyte content, at a constant soap concentration, will produce a three-phase condition in the centrifuge.

The method used to refine crude coconut oils is schematically shown in Figure 2. This process, utilizing a completely air-free pressurized system including Hermetic centrifuges (9), will allow control of the various conditions necessary to obtain a high refining yield. In this system both the oil and lye are separately preheated. The oil and proportioned reagent may be reacted in a high-speed, short-contact mixer, then immediately separated in the Hermetic centrifuge. The centrifugally separated refined oil then is pumped to the water-wash section. After mixing with water, followed again by centrifugal separation, the washed oil is vacuum-dried and pumped to storage.

Recent advances in centrifugal design have resulted in even more efficient separation at higher refining capacities per centrifugal unit. Figure 3 illustrates such a unit, the model SRG-214 high-capacity Hermetic centrifuge. This centrifugal with a disc bowl 24 in. in diameter may be used to refine, re-refine, or water-wash oils in the capacity range of 20,000 lbs. per hour which represents a capacity of eight tank cars per day per centrifugal. This machine has a built-in feed pump attached directly to the inlet of the hollow spindle.

In this case the preheated oil is initially contacted with the preheated lye in the spindle feed pump. The mixture is forced up the spindle and contacts the high-speed mixing device located in the upper portion of the spindle (10). This mixing device, termed Ultra-Short-Mix (3), allows a contact time of only a fraction of a second before separation of the oil from the soapstock. This separation, taking place in the Hermetic centrifuge, eliminates any possible contact with air. Air, especially in the case of coconut oil, will cause emulsions which will result in oil entrainment and lower yields.

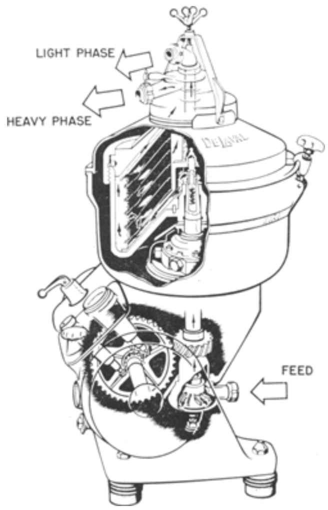

FIG. 3. High-capacity Hermetic centrifuge.

Conclusion

A continuous process for refining crude coconut oil has been described. This Hermetic system provides a means for continually controlling the variables of time, temperature, and reagent on a scientific, predictable basis. By utilizing the phase diagram as a guide for the correct conditions and employing a continuous process designed to maintain these conditions, it is always possible to obtain high yield refining results on crude coconut oil.

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[Received September 30, 1959]

Estimation of Unsaturation of Fats and Oils, Using Hypochlorous Acid

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HYPOCHLOROUS ACID has been successfully employed by Mukherjee (1) and Choudhury and Mukherjee (2) for the determination of unsaturation of oils containing both nonconjugated and conjugated unsaturation. One of the difficulties in the original method proposed by the above workers is the preparation of the hypochlorous acid reagent. This is usually done by passing a stream of washed chlorine through a 4N solution of sodium hydroxide, maintaining a temperature below 10°C., then diluting to 0.1N. It is a little difficult for ordinary commercial laboratories to prepare the above reagent.

It has been recently found by the present worker that commercial bleaching solutions sold in grocery stores, such as Clorox, serve very satisfactorily as a reagent in the determination of the unsaturation of oils. When Clorox is acidified with acetic acid, hypochlorous acid is liberated, which adds on to the double bonds quantitatively. The other substances present in Clorox do not interfere. By using Clorox, the most difficult step in the hypochlorous acid method for the determination of unsaturation of oils can be eliminated. The present method is much easier than the Wijs method, and it is believed that it is particularly suitable for commercial and industrial laboratories.

Experimental

A. *Fats and Oils Containing Nonconjugated Unsaturation*

Reagents

Clorox (or similar commercial bleaching agent); Clorox which was found to be 1.5N was diluted to 0.1N
Potassium iodide—15% solution
Sodium thiosulfate—0.1N solution
Starch indicator—1% solution

Procedure

Weigh 0.1–0.2 g. of oil into a 500-ml. glass-stoppered bottle and add 10 ml. of glacial acetic acid. Shake well to dissolve the oil, or disperse it thoroughly in the acid and add 25 ml. of 0.1N Clorox solution. Shake well again, and allow to stand for 10 min. at room temperature. Add 20 ml. of 15% potassium iodide solution, and after 1 min. titrate the liberated iodine in the usual manner, using 0.1N starch as an indicator. Prepare a blank simultaneously, containing no oil.

Calculation

$$\text{Iodine value} = \frac{(\text{ml. blank-ml. sample}) \times 0.127 \times \text{normality of thiosulfate}}{\text{wt. of sample}}$$

The iodine values of the following oils were determined by Wijs method, by using pure hypochlorous acid and also by using Clorox. The results are shown in Table I. It is seen that the Clorox method agrees very well with the Wijs method, also with the original hypochlorous acid method.

TABLE I
Iodine Numbers of Some Oils by Different Procedures

Oil used	Iodine number		
	Wijs method	Pure HO Cl	Clorox
Cottonseed	108.8	108.5	108.7
Soybean	129.5	129.2	129.3
Peanut	93.2	92.8	93.0
Sesame	110.9	111.2	110.9
Corn	120.7	120.8	120.5
Linseed	180.5	181.0	180.5
Beef tallow	42.8	43.1	43.0
Lard	65.2	65.1	65.2

B. *Fats and Oils Containing Conjugated Unsaturation*

Reagents

Clorox solution made to a 0.3N strength
Mercuric acetate, 2.5% in glacial acetic acid
Other reagents as above

Procedure

Weigh 0.1–0.2 g. of oil or fat into a 500-ml. glass-stoppered bottle, and add 10 ml. of a 2.5% solution of mercuric acetate in glacial acetic acid. Shake well to disperse the oil thoroughly. Add 25 ml. of 0.3N Clorox solution, and shake well again. Allow to stand for 1 hr. at approximately 20°C. Add potassium iodide and titrate as above, running a blank simultaneously.

Calculation

As above.

The iodine number of tung oil was determined by the following methods, as shown in Table II. The result by the Clorox method, also by the hypochlorous acid method, agrees fairly well with the catalytic hydrogenation procedure (3) and is comparable with the other accepted methods for the determination of total unsaturation of tung oil. The results are shown in Table II.