

METHOD OF REFINING AND STABILIZING  
MALAYAN COCONUT OIL

by

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# METHODS OF REFINING AND STABILIZING MALAYAN COCONUT OIL

## I. INTRODUCTION

Coconuts are grown in out-of-the-way places in the Malayan Peninsula; coconut oil is second only in importance to the natural rubber and the tin industries in this Peninsula. Wartime experience demonstrated the basic importance of the fats and oils for food. After World War II, the British Government introduced new plantation methods in Malaya in order to increase the production of coconut oil. In Malaya there are about 50 London companies operating coconut plantations, alone or in combination with rubber, and total coconut acreage is now one-sixth that of rubber, which is the industry of first importance. The money income from these three (rubber, tin, coconut) has been so great that the natives are no longer interested in the production of rice, which is the main food in the diet of the population in this Peninsula.

The climate of the Malayan Peninsula is considerably wetter and more humid than that of Ceylon and most of India. The temperature does not average much above 80°F., but the high humidity makes it difficult to endure. On the west coast, where the coconut plantations are principally located, the rainfall averages from 70 to 125 inches a year (36), coming mostly from September to January and again

from March to May, but continuing during the remainder of the year usually at the rate of several inches a month. The east coast has an even heavier precipitation because it gets the full sweep of the north-east monsoon off the China Sea.

In quality, Malayan copra ranks below that from Ceylon and India but above that of the South Sea Islands. It is in part sun-dried, but weather conditions necessitate very general use of artificial drying methods. The average yield of oil obtained by crushing dry copra is considered to be approximately 63 percent (3).

Before World War II, peanut oil and lard were the only two important cooking oils and fats used by the population of Malaya. The high free fatty acid content of coconut oil in Malaya is due to the drying of the copra by the crude and poorly controlled native method. However, free acids of coconut oil are very noticeable if present in considerable amounts, and they are sufficiently volatile and soluble to contribute a decided odor and flavor to the foods cooked in it. Due to this characteristic property, the edible value of coconut oil is greatly reduced.

Pigs grown in Malaya and other tropical zones usually have much more muscle than fat in their bodies. For this reason the price of lard is usually ten times the price of rice. Because of the limitation of cultivated



land, peanut production in Malaya is very low. Peanut oil is usually imported from China or India. Owing to the civil war in China and the food shortage in India after World War II, the importation of peanut oil into Malaya is very difficult. In addition, its price is five times that of rice, while coconut oil is one-half the price of rice.

For this study, 30 pounds of crude coconut oil were imported from a coconut oil plant in the Selangor State of Malaya.

The first purpose of the present investigation was to refine, bleach, and deodorize this crude coconut oil to produce an edible oil and make it possible to substitute it for peanut oil. The second purpose was to study the effectiveness of different antioxidants as stabilizers for the refined coconut oil.

## II. LITERATURE REVIEW

The World Production of Coconut Oil. The statistics relative to the production of vegetable oils are so generally inadequate that in many cases any estimate of world production can be regarded as little better than an intelligent guess.

The average yearly production of the principal edible plant oils and fats of commerce from 1934 to 1938 are shown in Table I (17).

Before 1940 (3) approximately 40 percent of the copra from Ceylon, 60 percent of that from the Philippines, 70 percent of that from British Malaya, and 95 percent of that from the Netherlands East Indies were exported for crushing.

According to Gruess (5), the United States imported in excess of 500 million pounds of copra in 1938, while the world production of copra was approximately 1500 million pounds at that time.

The Principal Uses of Coconut Oil. The principal use of coconut oil in the United States and in Europe is for the manufacture of soaps (3). Coconut oil is especially adaptable for soap making. There are a number of reasons for its popularity for soap making (36). Coconut

TABLE I

THE AVERAGE YEARLY PRODUCTION OF THE PRINCIPAL  
EDIBLE PLANT OILS AND FATS

Plant Oil	Quantity in 100 Million Pounds
Cottonseed Oil	30
Peanut Oil	30
Coconut Oil	25
Olive Oil	20
Soybean Oil	17.5
Palm Oil	12.5
Corn Oil	2.5
Palm-kernel Oil	7.5
Rapeseed Oil	7.5*
Sunflower Oil	7.5*
Sesame Oil	5.0*

\* Uncertain, estimate very approximate

oil (like palm-kernel oil, which it resembles very closely) contains a large proportion of lauric and myristic acid. The sodium compounds of these two acids are fairly soluble in water because of the short hydrocarbon chain length. Other fats and oils, particularly tallow and palm oil, are well adapted to soap making, but none except coconut and palm-kernel combines the qualities in a soap of solubility and hardness.

Formerly, a large volume of coconut oil found its way into margarine. However, its use in this product has declined greatly in recent years due to its short plastic range (3). A considerable quantity is consumed in confections and other edible products of a special nature. Because of its decided flavor and odor, its use in shortening has been largely reduced.

Chemical Composition of Coconut Oil. The chemical composition of coconut oil is tabulated in Table II.

Coconut oil contains a greater variety of fatty acids than most oils, but this variety is occasioned by differences in the molecular weights of saturated acids, rather than by differences in the degree of unsaturation of the acids. Normally, about 75 percent of total fatty acids of coconut oil consist of lauric, myristic, and palmitic acids. These acids melt at approximately  $44^{\circ}\text{C}.$ ,  $54^{\circ}\text{C}.$ , and  $63^{\circ}\text{C}.$ , respectively; consequently, there is a difference of only  $19^{\circ}\text{C}.$  between the melting points of the lowest and the highest of these three acids. On the other hand, the major fatty acids of high molecular weight fats are usually linoleic, oleic, palmitic, and stearic acids, which melt at  $-7^{\circ}\text{C}.$ ,  $16^{\circ}\text{C}.$ ,  $63^{\circ}\text{C}.$ , and  $70^{\circ}\text{C}.$ , respectively, with a difference of  $77^{\circ}\text{C}.$  between the lowest and the highest melting points in this group. The relatively narrow melting range

TABLE II  
FATTY ACID COMPOSITION OF COCONUT OIL

Fatty Acid	Percent
Saturated	
Caproic	0.5
Caprylic	9.0
Capric	6.8
Lauric	46.4
Myristic	18.0
Palmitic	9.0
Stearic	1.0
Unsaturated	
Oleic	7.6
Linoleic	1.6

of the coconut oil fatty acids is reflected in the glycerides and accounts for the limited plastic range of coconut oil. Unlike ordinary oils, coconut oil can be changed very little in its melting point and consistency by hydrogenation (3).

Standards for coconut oil as recommended by the American Oil Chemists' Society are tabulated in Table III (3).

TABLE III  
STANDARDS FOR COCONUT OIL

Specific Gravity at 99/15.5	0.869	-	0.874
Specific Gravity at 25/15.5	0.917	-	0.919
Refractive Index at 40°C.	1.448	-	1.450
Saponification value	250.0	-	264.0
Titer, °C.	20.0	-	24.0
Setting Point, °C.	21.8	-	23.0
Reichert-Meissel value	6.0	-	8.0
Polenske value	15.0	-	18.0

Refining, Bleaching, and Decolorization. The crude coconut oil produced from copra contains variable amounts of non-glyceride impurities. These impurities consist principally of free fatty acids. The fatty acids of coconut oil have a strong odor. It is essential that this oil should be rendered substantially void of free fatty acids by alkali refining before it is used in food products.

Willem (39) employed a process to neutralize the free fatty acid of coconut oil with  $\text{NH}_3$  and multistage counter-current extraction with aqueous isopropyl alcohol.

In 1937, Schmidt (34) used aliphatic carbodiimides for deacidification of coconut oil. The velocity of deacidification depends upon the temperature at which the

carbodiimides act on the free acids. The amount of carbodiimides required for complete deacidification can be calculated from the amount of alkali required to neutralize the oil.

In general, refining by means of alkalies is widely used in almost all the edible fat and oil industry. According to Bailey (3) and Hilditch (14), there are several methods used in alkali refining. However, the following two methods are usually employed.

Refining by the dry method. This is the one generally practiced in the United States where any kind of fat or oil is refined by means of caustic soda. In this method the oil is treated with relatively strong lye, and the soap-stock or "foots" is recovered in a solid or semisolid form from the cooled oil. This method has the advantage of being rapid and convenient and produces a concentrated soap-stock.

Refining by the wet method. In this method the soap-stock is washed to the bottom of the refining kettle with considerable quantities of water, and recovered in the form of a fluid solution. Coconut oil is usually refined by the wet method.

The object of bleaching is to remove coloring materials which are relatively unaffected by refining. This

treatment usually consists of bringing the oil into contact with a solid adsorbent having an affinity for the coloring materials. Bleaching is normally carried out after refining and prior to hydrogenation or deodorization. The most important adsorbent used in bleaching fats and oils is bleaching earth or clay. Besides bleaching clay, the only adsorbent widely used in edible oil industry is charcoal or carbon. Carbon is very effective in removing the "bloom" caused by traces of mineral oil in vegetable oils (3).

Dunnire (6) purified coconut oil by vacuum treatment with a solid adsorbent. The mixture is heated in a range of approximately 150 to 300°F. A vacuum of 27 to 30 inches of mercury is used. The adsorbent which may be bone black, charcoal, Fuller's Earth, carbon black, or the like. The oil treated by this method has better color and lower ash content.

Gallay (11) investigated Canadian bentonites as refining and bleaching agents for coconut oil. Low silicon dioxide to aluminum oxide ratio and a high percentage of combined water are the outstanding characteristics of modern bentonites.

Deodorization is a process which is used to remove the substances giving rise to odors and flavors. Salway (31) stated that certain ketones, notably methyl nonyl



ketone, are the compounds responsible for tastes and odors in coconut oil. Bailey (3) mentioned "the flavor and odor removal is observed to generally parallel free fatty acid removal in oils". It is probable that the vapor pressures and molecular weights of the odoriferous substances are the same as those of the common fatty acids of 12 to 18 carbon atoms.

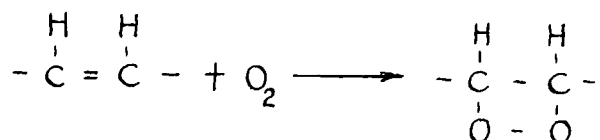
The steam decolorization method is the most common method used in the edible fat industry. According to Bailey (3), various methods other than decolorization have been proposed for rendering edible oils odorless and tasteless, but none, as far as he is aware, have ever found commercial application.

Rancidity of Oils and Fats. Atmospheric oxidation of oils may be divided into two sharply differentiated phenomena, namely oxidation accompanied by polymerization which occurs in highly unsaturated oils such as tung oil, and oxidation in less unsaturated oils such as cottonseed oil, coconut oil, etc., which leads to the development of rancidity. According to Bailey (3), distinctive and unpleasant odors and flavors form as rancidity develops.

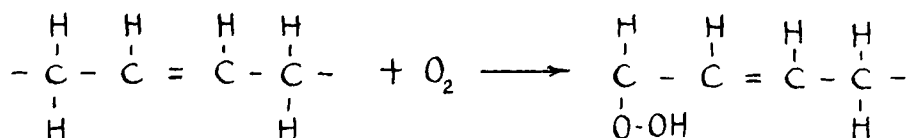
The development of rancidity is a surface phenomenon involving only a small portion of the oil. Not more than 0.1 percent of the fat may actually decompose to form the

volatile, low molecular weight compounds responsible for rancid flavor and odor (3).

The initial step in the oxidation of a fat is the addition of oxygen at or near the double bond of a fatty acid chain to form unstable compounds which are generally designated as peroxides (3, 19).



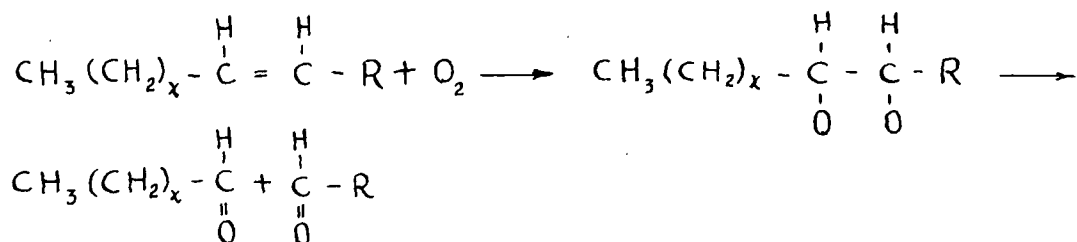
Farmer and co-workers (8) have demonstrated that in the case of unconjugated fatty acids oxidized at ordinary temperature, the initial oxidation products consist of hydroperoxides, which are formed by the addition of oxygen at a carbon atom adjacent to the double bond, and leave the latter intact.



Atherton and Hilditch (2) concluded that the formation of hydroperoxides predominates at lower temperatures, but that there is little formation of these compounds at higher temperatures. Whatever their structure, the peroxides, etc., are but intermediate and transitory products in the general course of oxidation.

The typical sharp taste and the unpleasant odor of

the rancidity, according to Bailey (3), is believed to be chiefly due to the presence of aldehydes of medium molecular weight, particularly heptylic and nonoic aldehydes. These compounds may be formed by the oxidation and breaking of a fatty acid chain at a double bond.



An oil and fat consists of complex mixture of glycerides which are built up from glycerol in combination with saturated and unsaturated fatty acids. Under ordinary conditions, saturated fatty acids are stable in air. Myristic acid, for example, does not oxidize on heating for 25 hours in oxygen at 90°C. (19). However, under the influence of the peroxides present in a mixed fat, a certain amount of oxidation of the saturated fatty acids also occurs.

Free oxygen, in the presence of short-wave ultraviolet light or of metallic catalysts at elevated temperatures, is known to oxidize saturated acids directly (19).

Susceptibility to oxidation is influenced also to some extent by molecular structure. The greater the number of double bonds the more reactive the fat or oil towards oxygen. For example, linoleic acid oxidizes much

more rapidly than oleic acid under the same conditions, while the introduction of a hydroxyl group into the oleic acid chain to form ricinoleic acid results in a great decrease in susceptibility to oxidation, because the hydroxyl group retards oxidation (15).

Fatty acids in the free form are generally inclined to oxidize more readily than when combined as glycerides (3). Certainly the development of a moderate amount of free fatty acids in a sample does not affect its stability to any large degree.

Two periods in the oxidation of fat are usually discernible:

1. The initial period or induction period.

In this period, relatively slow oxidation of the fat takes place at a more or less uniform rate.

2. The second period.

After the first period, oxidation of the fat proceeds at a greatly accelerated rate.

Methods used in the determination of rancidity of fat and oil. Up to the present time, there are various methods which have been developed for determining the rancidity of fats and oils. Rancid odors and flavors may be tested organoleptically, or rancidity may be determined by

chemical methods. The Kreis color test, originally described in 1902, has been used for many years to detect oxidative rancidity, although a positive Kreis test in the crude oil may be due, not to decomposition products in the oil, but to substances derived from the seed from which the oil was obtained (8). The Kreis color test is due to the presence of epihydrin aldehyde,  $\text{CH}_2=\underset{\text{L-O-}}{\text{CH}}-\text{CHO}$ , and unless this aldehyde is present the product will not give a positive Kreis test. Lea (19) states that the limit of sensitivity of this test is at a concentration of one part of aldehyde in about four million parts of oil.

The Schiff test is a qualitative test for aldehydes. The quantitative methods of Iasoglio and Kerr (18) depend upon the presence of low molecular weight, steam-volatile aldehydes, whereas that of Schibsted (33) is for aldehydes of high molecular weight. The bisulfite method of Lea (19) is adapted particularly for the estimation of aldehydes of medium molecular weight. Of the chemical methods for determining the development of rancidity the iodometric method is the most sensitive. The peroxides formed in the fat or oil are intermediate and transitory products. They are highly reactive, and quickly decompose or combine with one another in a variety of poorly understood reactions, to yield the compounds actually responsible for rancid flavors and odors. They are estimated through their ability to

liberate iodine from potassium iodide in glacial acetic acid solution. The peroxide value of a fat or oil is measured as millimoles of oxygen or milli-equivalents of oxygen per 1000 grams of fat or oil. As Watts (38) points out, the former unit is preferred.

Grant and Lips (13) have reviewed the chemical methods available for the measurement of the development of rancidity and have tabulated the correlation coefficients for these chemical tests and the organoleptic test. Lard was used as the substrate in these latter evaluations. Lundberg (23) also has compiled an excellent review of "methods used in measuring rancidity and stability", as well as a review of the "stabilization of fats by means of antioxidants".

### III. EXPERIMENTAL STUDY

Analysis of Crude Coconut Oil. The crude coconut oil was received from Malaya in tin containers. The oil was stored in the original containers at 34°F. Analyses for free fatty acids, iodine value, saponification number, moisture content, and specific gravity were completed on the crude coconut oil. Detailed results are tabulated in the next chapter.

The free fatty acids were determined according to the official method of the American Oil Chemists' Society (30). In all these titrations for free fatty acids, 0.1860 normal sodium hydroxide solution was used. For coconut oil, free fatty acids are calculated as percent lauric acid.

The iodine value is the number of grams of iodine absorbed by 100 grams of the oil. In these titrations for iodine value, 25 ml. of the standard iodine solution were equivalent to 26.87 ml. of 0.1091 normal sodium thiosulfate solution.

The saponification number is defined as the number of milligrams of potassium hydroxide required to saponify one gram of the crude coconut oil. Alcoholic potassium hydroxide (normality 0.5706) was used in the saponification reaction, and the excess was back titrated with 0.4135 normal hydrochloric acid solution.

Determinations for the iodine value, saponification number, moisture content, and the specific gravity were carried out according to the methods of analysis of the Association of Official Agricultural Chemists (1).

Peroxide Value. A modification of the original method developed by Lea (19) was used for determining the peroxide values of coconut oil. The sample was analyzed in the following manner.

1. The sample was weighed (1.000 gram plus or minus 0.05 gram) into an amber glass test tube.
2. One gram of powdered potassium iodide was added.
3. 20 ml. of a 2:1 mixture by volume of glacial acetic acid and carbon tetrachloride were added.
4. The test tube containing the above mixture was placed immediately in boiling water and heated exactly one minute. Precautions should be taken to avoid foaming over the top of the test tube.
5. Then the mixture in the tube was poured into a 125 ml. Erlenmeyer flask and the tube was washed out with 30 ml. of distilled water.
6. The free iodine was titrated with 0.02 normal sodium thiosulfate solution until near the end-point.
7. Then two ml. of starch solution were added and



the titration was continued until the end-point (colorless solution) was attained.

From the data the peroxide value was calculated both as millimoles and milliequivalents of oxygen per 1000 grams of the oil. These values are tabulated in Table V.

### Purification Procedures

1. Refining. The principal object of refining is the removal of the impurities in addition to the free fatty acids. The impurities present in all natural oils may be:

- a. Relatively coarse suspended matter, including mucilage (vegetable or animal tissue), albuminous matter, and resinous bodies.
- b. Exceedingly fine suspensions of colloiddally dispersed matter.
- c. Natural coloring matters.
- d. Free fatty acids produced by hydrolysis from the natural oil.
- e. Semi-volatile compounds dissolved in the fat. These produce in it an undesirable characteristic odor and taste.

In coconut oil, the most important impurity is free fatty acids.

For years the well-known refining kettle or batch method was used to mix in the alkali solution with crude

oil, agitate, heat, and separate it into the two-phase oil and soapstock condition. Then the latter would settle freely and compactly so as to avoid entrainment of the neutral oil. The most effective and hitherto almost universally used agent for accomplishing this action was sodium hydroxide. This reagent is a strong base and is very effective for vigorous action on these impurities. However, it attacks neutral oil. Usually an excess of sodium hydroxide solution must be employed in order to obtain a complete removal of the impurities, including an adequate percentage of the color bodies. The excess is sometimes responsible for the loss of some of the neutral oil. In addition to the loss of neutral oil through the direct decomposition by the sodium hydroxide, there is a loss of neutral oil occasioned by the occlusion, entrainment, and the entrapment of the neutral oil in the formation of soapstock and the subsequent removal of soapstock from the refined oil (24).

In recent years, Mattikow (24) has investigated a new method of refining oils with non-saponifying alkalies. This is the so-called Clayton Process. In this process, a neutralizing agent which does not combine with neutral oil is used. Sodium carbonate (called soda ash by the trade) is an alkali answering this purpose. Sodium carbonate has two advantages over sodium hydroxide:

- a. It is cheaper than sodium hydroxide.
- b. It does not attack neutral oil.

However, the reagent has many drawbacks:

- a. It neutralizes the free fatty acids with a sudden release of carbon dioxide which slows the rate of settling of the soapstock and increases the volume.
- b. It attacks the coloring substances insufficiently.
- c. It forms emulsions readily during the increase-in-volume stage.

In 1942 the new Clayton Process was perfected sufficiently to be used commercially for the removal of the impurities from crude oils. This process produced neutral oil with a low refining loss. The principles of the Clayton Process are dehydration of the oil and soapstock under high vacuum and then rehydration with soda ash reagent to facilitate removing the soapstock from neutralized oil (24).

According to Fash (9), the hitherto unexplainable results obtained in the refining of vegetable oils are understandable from the following theoretical concepts:

- a. The color particles and colloidal substances present in crude oils are in colloidal suspension by reason of positive electrical charges.
- b. The soap formed in the refining process is

negatively charged. These negative charges neutralize the positive charges on the color particles and colloidal substances in suspension in the oil. As a result of this action, flocculation of these impurities takes place in the soapstock.

c. When these positive charges are neutralized, the electrically neutral color particles and colloidal substances are soluble in the oil. The solubility rate and the absolute amount dissolving are dependent upon the pH, temperature, reaction time, and degree of agitation.

Refining of the coconut oil was carried out experimentally in the following manner: A quantity of soda ash (1.3% for this oil) which is equivalent to twice the free fatty acid content of the crude oil is dissolved in 10 ml. of boiling water and transferred to a 600 ml. beaker. 400 grams of oil, previously heated to 80°C., are poured cautiously into the carbonate solution with continuous agitation. The rate of addition is governed by the volume of carbon dioxide liberated during the neutralization process. A constant speed electric stirrer is useful for agitation. Heat may be applied cautiously during the addition of the oil until the temperature reaches 100°C., the agitation being continued for 20 minutes and then stopped. In this process, the water is removed by evaporation, and

the soap thus formed is relatively dry and rises to the top of the oil in a thick layer. The oil was filtered by vacuum through a Whatman filter paper (Number two). The refining loss was calculated. In addition, the free fatty acid content of the refined oil was determined. This information is tabulated in Table VI.

2. Bleaching. Crude fats and oils contain many kinds of coloring substances in colloidal dispersion and in true solution. Colloidal substances are removed usually during alkali refining. The dissolved pigments are not particularly objectionable, but the consumer prefers a fat or oil with a light color. Therefore, a suitable process for the decolorization of the oil must be applied. The combination of color and pigments are different for each fat and oil depending to a large extent upon the character and quality of the original oil-bearing material. In general, red and yellow colors are due mainly to various carotenoid pigments such as carotenes and xanthophylls and to their isomers, as well as to their decomposition products (35). These colors can be removed by bleaching clays and activated carbon. The bleaching clays were grouped into three general classes (37):

- a. Acid-activated clays
- b. Neutral Earth
- c. Material high in silica content.

For coconut oil, the yellow pigments can readily be removed by Fuller's Earth, while the red pigments can be removed with a small percentage of activated carbon (35).

In the edible oil industry it has been found that activated carbons will correct off-flavored oils and "earthy" flavor imparted by Fuller's Earth. It has been found that activated carbon will remove completely the last traces of soap from oils. At the same time, the free fatty acids in the oil are reduced considerably.

Factors which influence the action of an activated carbon are temperature, time of contact, speed of agitation, pH of the solution, and degree of decolorization of the oil.

Factors which influence the choice of a bleaching clay include oil retention value, filtration characteristics, tastes imparted to the oil, and cost. In addition, the effect of the clay on the reduction of the free fatty acid content in the oil is an important consideration.

In bleaching the oil five different treatments were applied:

- a. Two parts of Norite plus four parts of Fuller's Earth.
- b. Six parts of Fuller's Earth.

- c. One part of Norite plus five parts of Fuller's Earth.
- d. Six parts of Fuller's Earth (0.1 ml. of 0.1%  $H_2SO_4$  added).
- e. Two parts of Norite and three parts of Fuller's Earth.

These amounts were used for each 100 parts of the oil.

Bleaching was carried out in these various treatments by the standard procedure (30). After filtering, the transmission of each treated sample, as well as that of the crude oil, was measured in a Lunetron at 450 mμ., and the results are shown graphically in Figure I.

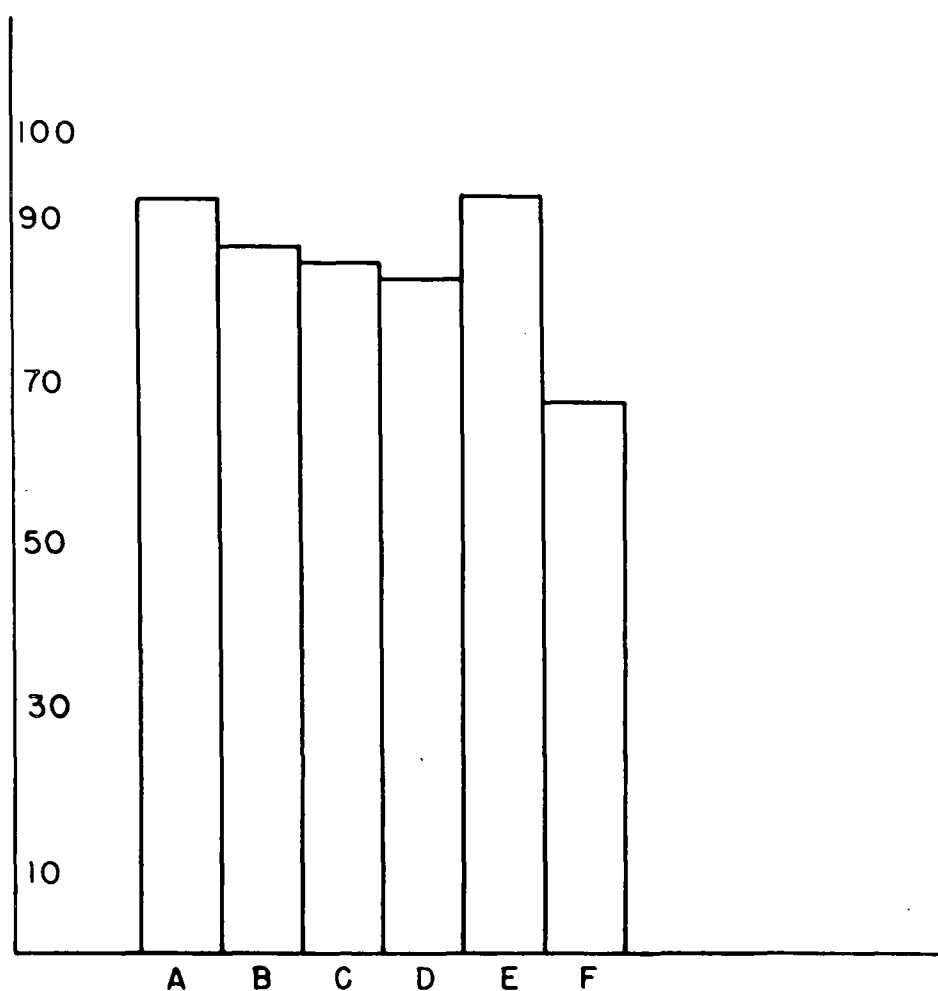
Decolorization. Odorless and tasteless fats and oils are demanded more highly on the market than those with a decided odor or flavor. After refining and bleaching, coconut oil still imparts a decided flavor and odor to foods cooked with this oil. Hence it is necessary to decolorize this oil for edible purposes.

The basic principle of decolorization process is simple, consisting essentially of the removal by fractional distillation of the minute amounts of the odoriferous substances from the oil with the minimum of injury to the oil itself. The odoriferous substances to be

FIGURE 1

PERCENT TRANSMISSION OF BLEACHED  
OIL (WAVE LENGTH 450 M $\mu$ )

F — CRUDE COCONUT OIL





removed are generally considered to be ketones and aldehydes. The presence of methyl nonyl ketone has been identified as a constituent of coconut oil and palm oil (35, 31).

As a rule this process is carried out after the free fatty acids have been removed and after any necessary bleaching action has been performed. The oil is heated in a closed iron or aluminum vessel to a temperature of about 160-220°C. by means of high-pressure steam in closed coils. The deodorization reaction is run under reduced pressure (48 mm.), and steam is passed through coils at the bottom of the vessel. So essentially, the method depends on steam distillation at a high temperature and under reduced pressure to remove the volatile substances. In the laboratory this was done in pyrex glass equipment. The results for the bleaching and the deodorization are summarized in Table VII.

## IV. RESULTS OF THE ANALYSIS AND PURIFICATION

The detailed results on the analysis of crude coconut oil are summarized in Table IV.

TABLE IV  
ANALYSIS OF CRUDE COCONUT OIL

Weight of Oil (grams)	Ml. of Standard Solution Used	Percent Free Fatty Acids
7.3476	1.30	0.65
8.9128	1.50	0.62
9.4050	1.65	0.65
10.0597	1.80	0.65
50.2630	9.00	0.65
Iodine Value		
0.2926	1.42	6.76
0.3764	1.80	6.70
0.4774	2.12	6.70
Saponification Number		
4.4591	17.92	253
5.1314	8.89	252
5.1987	8.61	251

TABLE IV (continued)  
ANALYSIS OF CRUDE COCONUT OIL

Original Weight	"Dry" Weight	Percent Moisture
5.1730	5.1690	0.116
6.9186	6.9121	0.122
Weight of Sample at 37°C.	Weight of Water at 37°C.	Specific Gravity at 37°C.
22.5737	24.6909	0.9142
22.6940	24.6950	0.9149

From calculations, the specific gravity at 25°C. was determined as 0.9285 and 0.9292, respectively. The average value at 25°C. is 0.9288

The peroxide values for crude and refined coconut oil are summarized in Table V.

TABLE V  
PEROXIDE VALUES FOR COCONUT OIL

Condition of the Oil	Sample Weight in Grams	Ml. of 0.02 Normal Thiosulfate Solution	P.V. in Millimoles	P.V. in Milli- equivalents
Crude	1.0130	0.05	0.5	1.0
	1.0270	0.05	0.5	1.0
Refined and Bleached	1.0314	0.17	1.65	3.3
	1.1012	0.18	1.6	3.2
Refined, Bleached, and Deodorized	1.0043	0	0	0
	1.1120	0	0	0

The refining losses and the free fatty acid content of the refined oil are tabulated in Table VI.

TABLE VI  
REFINING OF COCONUT OIL

Weight of Crude Oil in grams	Weight after Refining	Percent Loss
400	387.5	3.0
475	460.	3.0
500	485.	3.0
Weight of Refined Oil	Ml. of Standard Sodium Hydroxide Solution	Percent Free Fatty Acid
50.1728	1.25	0.09
50.2100	1.25	0.09
50.2344	1.3	0.09

The summary of the data on the vacuum decolorization procedures for the refined and bleached coconut oil is tabulated in Table VII.

TABLE VII  
DEODORIZATION OF COCONUT OIL

Bleaching Treatment (See Page 24)	Temperature °C.	Time (minutes)	Reaction
a	120	60	No color change Coconut odor remains
b	120	60	Slight color change Coconut odor remains
c	120	60	No color change Coconut odor remains
d	120	60	Color changes to yellow Coconut odor remains
e	120	60	No color change Coconut odor remains
a	120	90	No color change No coconut odor
b	120	90	Slight color change Slight coconut odor
c	120	90	No color change Slight coconut odor
d	120	90	Color changes to brown Slight coconut odor
e	120	90	No color change No coconut odor
a	140	60	No color change No coconut odor
b	140	60	Color changes to brown No coconut odor
c	140	60	Slight color change No coconut odor

TABLE VII (continued)

## DEODORIZATION OF COCONUT OIL

Bleaching Treatment (See Page 24)	Temperature °C.	Time (minutes)	Reaction
a	140	60	Color changes to brown No coconut odor
e	140	60	Slight color change No coconut odor
a	160	60	Color changes to brown No coconut odor
b	160	60	Color changes to brown No coconut odor
c	160	60	Color changes to brown No coconut odor
d	160	60	Color changes to brown No coconut odor
e	160	60	Color changes to brown No coconut odor

## V. STABILIZATION OF COCONUT OIL

In general, the Schaal oven test is a simple and widely used method for determining the stability of fats and oils. There are several reasons why this test is today one of the most widely used methods for evaluating the stability of oils and fats and for products containing oils or fats (28).

- a. The method is simple.
- b. It requires a minimum of equipment.
- c. The test can be conducted with a reasonable degree of success by persons having little or no technical knowledge.
- d. The result is expressed simply as "days" required to become "rancid".
- e. The test provides a means of comparing the "shelf life" of fats and oils.

The Schaal oven test was the method used in these experiments to determine the stability of crude and refined coconut oil. In the test, 50 grams of the oil were placed in beakers of 250 ml. capacity. The beakers were then covered with watch glasses and placed on the shelf of an air oven. The temperature of the oven was regulated at 63°C. The samples were smelled daily, in the morning, for rancid odor, and 1.1 ml. of both refined and crude oil were



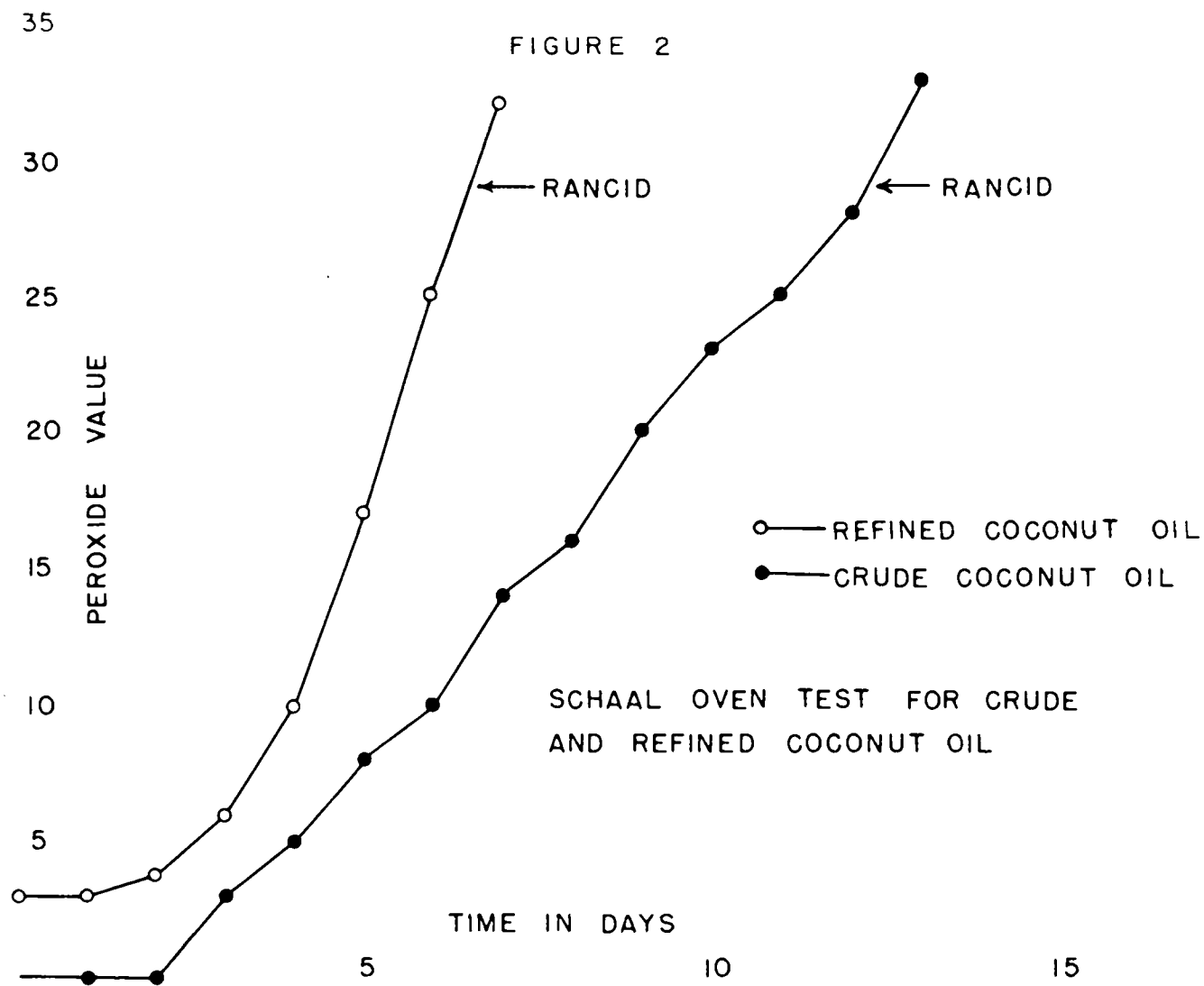
taken daily by a graduated one ml. pipette for the determination of the peroxide value. The stability of both refined and crude coconut oil is shown graphically in Figure 2. The refined oil used in these tests was the oil which was bleached by treatment "e" (see page 25) and then deodorized under vacuum at 120°C. for one and one-half hours.

The role of antioxidants in the stabilization of fats is to inhibit temporarily oxidative reaction. A remarkable characteristic of antioxidants is their great effectiveness in low concentration in the fats and oils. Above an optimum concentration they are inclined to act as pro-oxidants (3, 19, 23).

Antioxidants were used in these experiments to stabilize refined coconut oil. Not all antioxidants possess the same stabilizing properties in coconut oil. A screening test was used to choose those antioxidants which were most effective in stabilizing coconut oil.

In these tests, the proper antioxidant in the desired concentration was dissolved in 100 grams of the processed oil. Then 20 ml. of sample were transferred to a 50 ml. beaker, covered with a watch glass, and placed in the air oven (Temperature 63°C.).

Every morning the odor of each sample was checked. At the first sign of any change in odor, the peroxide value



of the sample was determined. As soon as a sample showed definite signs of rancidity in the organoleptic testing, it was sampled right away, and the peroxide value was determined. It was noted that under these conditions the peroxide value had attained or exceeded 29. The effectiveness of different antioxidants in this screening test are summarized in Table VIII. It should be noted that the protection factor is the ratio of the keeping time of the sample with antioxidant added to the keeping time of the control (23). Conditions such as size and surface area of the sample must be carefully controlled if reliable results are to be obtained. These and other factors are stressed by Ewbank and Gould (7).

TABLE VIII  
THE EFFECTIVENESS OF DIFFERENT ANTIOXIDANTS  
FOR REFINED COCONUT OIL

Parts of Antioxidant in 100 Parts of Coconut Oil	Stability in Days	P.V.	P.F.
0.005 NDGA	14	31	2.8
0.01 NDGA	16	29	3.2
0.005 NDGA and 0.005 Citric Acid	15	31	3.0
0.005 NDGA and 0.01 Citric Acid	18	30	3.6
0.01 NDGA and 0.005 Citric Acid	30	32	6.0
0.01 NDGA and 0.01 Citric Acid	30	31	6.0
0.005 NDGA and 0.005 $H_3PO_4$	28	32	5.6
0.005 NDGA and 0.01 $H_3PO_4$	24	30	5.8
0.01 NDGA and 0.005 $H_3PO_4$	30	29	6.0
0.01 NDGA and 0.01 $H_3PO_4$	36	33	7.2
Refined oil (control)	5	31	1.0
Crude coconut oil	11	34	-
0.01 Citric acid	21	34	4.5
0.01 $H_3PO_4$	25	32	5.0
0.01 Citric acid and 0.01 $H_3PO_4$	36	32	7.2
0.01 Ascorbyl Palmitates	20	32	4.0
0.01 Ascorbyl Palmitates and 0.01 NDGA	30	30	6.0
0.01 Propylene Glycol	22	30	4.5

TABLE VIII (continued)  
THE EFFECTIVENESS OF DIFFERENT ANTIOXIDANTS  
FOR REFINED COCONUT OIL

Parts of Antioxidant in 100 Parts of Coconut Oil	Stability in Days	P.V.	P.F.
0.05 Propylene Glycol	22	29	4.5
0.005 Hydroquinone and 0.005 Propylene Glycol	21	29	4.2
0.005 Hydroquinone	Over 40	-	-
0.01 Hydroquinone	Over 40	-	-
0.005 G-4	Over 40	-	-
0.01 G-4	Over 40	-	-
0.05 Tocopherol	Over 40	-	-
0.01 Tocopherol	Over 40	-	-
0.005 Gallic Acid	Over 40	-	-
0.01 Gallic Acid	Over 40	-	-
0.005 Gum Guaiac	Over 40	-	-
0.01 Gum Guaiac	Over 40	-	-
P.V. = Peroxide value.      P.F. = Protective Factor			

The best five antioxidants as measured by stability units in the screening test (See Table VIII) were used in this experiment to determine the stability of refined coconut oil. The procedure as outlined on Page 34 was followed. The results are summarized in Table IX. It should be noted that G-4 is a commercial antioxidant containing a mixture of propyl gallate, phospholipids, corn oil, and citric acid.

TABLE IX  
THE EFFECTIVENESS OF FIVE SELECTED ANTIOXIDANTS  
FOR REFINED COCONUT OIL

Parts of Antioxidant in 100 Parts of Coconut Oil	Stability in Days	P. V.	P. F.
0.005 Gallic Acid	50	31	8.3
0.01 Gallic Acid	-	-	-
0.005 G-4	55	32	9.1
0.01 G-4	65	30	10.8
0.01 Gum Guaiac	49	30	8.1
0.1 Gum Guaiac	52	33	8.6
0.005 Hydroquinone	52	30	8.6
0.01 Hydroquinone	-	-	-
0.005 Tocopherol	49	35	8.1
0.01 Tocopherol	51	33	8.5
Control Sample	6	30	1.0

## VI. DISCUSSION

The average loss of crude coconut oil after deacidification by soda ash was three percent, and the free fatty acid content was reduced from the original 0.65 percent to 0.09 percent.

Mixtures of Norite and Fuller's Earth have been used to bleach the coconut oil. The percentage transmission (450 mμ.) after different treatments was measured in the Lumetron (See Figure 1). A white oil was developed when 100 parts of the coconut oil were bleached with two parts of Norite and three parts of Fuller's Earth. Norite has the power to remove off-flavors from coconut oil and also will remove "earthy" flavor imparted by the Fuller's Earth.

Vacuum deodorization (48 mm.) for 90 minutes at 120°C. produced an edible oil with good color.

The Schaal oven test was used in these experiments for determining the stability of coconut oil at 63°C. A temperature lower than 63°C. would be preferable for the study of the development of rancidity, since it would approach more closely normal storage conditions for coconut oil in Malaya (about 40°C.).

Data in Figure 2 and Table VIII showed that the organoleptic test for rancidity became positive when the peroxide value exceeded twenty-nine. In addition, data in

this same table brought into sharp focus that not all antioxidants are suitable for the prevention of rancidity development in coconut oil. Nordihydroguaiacetic acid with four phenolic groups per molecule has the ability in low concentrations to markedly inhibit the autoxidation of fats and oils (10, 22). However, in these tests NDGA is a poor stabilizer for coconut oil.

Hydroquinone exhibited good protective action in these experiments. Because of its supposed toxicity, it has not been used in edible fats or oils. However, it is usually used for purposes of comparison in studies of other antioxidants (23).

Gum guaiac was the first antioxidant to be approved for use in lard by the Meat Inspection Division of the Bureau of Animal Industry in 1940 (4). In this test, gum guaiac was added to the deodorized coconut oil by means of an acetic acid solution. Then the acetic acid was removed by vacuum evaporation at 80°C. According to Lundberg, gum guaiac was more effective in animal fats than in vegetable oils (23). In this test, the oil turned slightly brown when it became rancid.

Gallic acid is a powerful phenolic antioxidant in itself. It is a highly effective inhibitor of rancidity development in both animal and vegetable oil (23, 26). In these experiments it was an excellent antioxidant for



coconut oil. Although gallic acid is inexpensive and effective, its use has not been approved, presumably because it has not been shown to be non-toxic.

Tocopherols are important and universally distributed antioxidants in natural fats and oils (3, 4). It has long been recognized that, due to the presence of minute amounts of these substances capable of powerfully inhibiting oxidation, natural fats and oils are much more resistant to deterioration than processed fats and oils. In these tests a tocopherol concentrate behaved as a fairly good antioxidant for the coconut oil. Concentrations of either 0.005 percent or 0.01 percent have almost the same effectiveness.

Decreasing the size of the sample or increasing the surface area exposed markedly increases the rate of oxidation (7). Data obtained from Tables VIII and IX showed that 20 ml. of oil placed in a 50 ml. beaker became rancid sooner than 58 ml. of oil (50 grams) placed in a 250 ml. beaker under the same conditions. Thus, in the oxidation studies, standardization of the size of sample and container was important if comparable results were to be secured.

## VII. SUMMARY

Two parts of Norite and three parts of Fuller's Earth produce excellent results in the bleaching of crude coconut oil.

Deodorization of the bleached coconut oil at 120°C. for 90 minutes under vacuum (48 mm.) was found to be most satisfactory.

The Schaal test conducted at 63°C. was found to be a satisfactory method for determining the stability of coconut oil under these accelerated conditions.

The organoleptic test for rancidity became positive when the peroxide number of the coconut oil exceeds twenty-nine.

In the Schaal test the size of the sample and the size of container must be considered for reliable results.

Gallic acid, G-4, gum guaiac, hydroquinone, and a tocopherol concentrate are good antioxidants for coconut oil.

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