

# Degumming, Refining, Bleaching, and Deodorization Theory

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## ABSTRACT

Basic theory and principles of degumming, refining, bleaching, and deodorization are reviewed. Composition of crude oils, hydration of ions and molecules, neutralization of organic acid, and separation and modification of products by centrifugation, adsorption, and vacuum steam distillation are briefly summarized. Reactions of vegetable oils include hydration, neutralization, and oxidation.

## INTRODUCTION

A variety of procedures which include both reactions and physical separations may be involved in the conversion of crude vegetable oil to an edible product. The important reactions are hydration of phospholipids in degumming, the neutralization of free fatty acids with alkali, and the autoxidation and cyclization of pigments to remove color. Deliberate attempts are made to reduce autoxidation to a minimum, but it usually occurs to the detriment of the oil. Hydration occurs whenever water is mixed with crude oils or when free fatty acids are neutralized. More important than the reactions are the physical separations that occur by centrifugation in degumming and alkali or other refining, adsorption in bleaching, and vacuum steam distillation in deodorization.

## COMPOSITION

Of primary importance in the refining of any oil is its composition. Although most fatty materials of similar origin can be converted to edible products by similar procedures, the composition of the particular starting material or crude oil is a determining factor. Some of the many materials present in a crude oil are triglycerides, free fatty acids, sterols, tocopherols, phospholipids, pigments, oxidized products, and waxes.

The triglycerides or triacyl glycerols constitute over 95% of most crude oils, and they are the material that we wish to purify. However, we must not do so to the extent of removing all of the other minor components. Usually, free fatty acids, phospholipids, pigments to some degree, oxidative products, and waxes are the only materials that need be removed. Sometimes it is not necessary to be concerned with pigments, waxes, and oxidation products. The major concern is usually with free fatty acids and phospholipids.

The amount of free fatty acids present is a measure of the quality of the unrefined as well as the refined oil. If it is too high, alternate procedures or alternate inedible uses should be sought.

Free fatty acids are lowered by refining, such as with alkali, or by other methods. An excess of alkali is added over the amount necessary to neutralize the free fatty acid present. The suspension or solution which results is usually separated by centrifugation. Vacuum steam distillation can also be used to separate free fatty acids provided the amounts are not too high and phospholipids are low.

Pigments present in vegetable oils include carotene (CH), xanthophyll (CHO), chlorophyll (CHNO), gossypol (polyphenol), chroman-quinone, diketones, and browning products. Many different materials are included under this heading, including  $\alpha$ -,  $\beta$ -, and  $\gamma$ -carotene. These are conju-

gated hydrocarbons with isoprene units that will heat bleach and oxidize readily. Their conjugation imparts an orange to red color. Oxidation or heating removes this color. Indeed, oxidation of the central double bond changes red to yellow color. Xanthophylls are oxygen "analogs" of the carotenes. Other pigments may assume a major importance in some oils, e.g., gossypol in cottonseed oil, chlorophyll in green soybean oil, and  $\alpha$ -tocopherol in a number of oils.  $\alpha$ -Tocopherol oxidizes to a very colorful chroman-quinone. Chlorophyll is better removed before alkali treatment since chlorophyll tends to be stabilized by alkali and heat and harder to remove. Oxidation can also lead to yellow diketones and brown colors.

The phosphatides in oils like soybean oil often receive special treatment. Their main classes are phosphoglycerides, phosphoinositides, and phytosphingosines. The ionic structure of phosphatidyl choline and ethanolamine are shown in Figure 1. These phospholipids are nature's emulsifiers and find many uses. Their ionic structures readily hydrate to permit removal by centrifugation.

If waxes are a problem, they are usually removed by winterization (cooling and filtering).

## SEPARATION AND REACTIONS

The primary methods used in separations are centrifugation as already mentioned in removal of pigments, and vacuum steam distillation for the removal of oxidative cleavage products (odors and flavors) and free fatty acids. Reactions involved include hydration as already mentioned under phospholipids, neutralization with alkali to form soaps (acids are sometimes used in refining but will not be discussed in this paper), and oxidation which should be avoided but usually occurs in sufficient amounts to bleach or improve the color of the oil.

Hydration occurs with the ionic part of the phospholipid molecule, but many ions are hydrated in presence of water. Table I lists some of the ions that may occur in the hydration and refining of an oil. The hydrogen ion ( $H^+$ ) is often cited as being  $H_3O^+$ , but it is more likely to be  $H_9O_4^+$  or even higher in water.

Oxidation usually occurs between the unsaturated bonds in the oil to form hydroperoxides. Autoxidation of oleic ester is shown in Figure 2. Four different hydroperoxides are formed. These decompose to form some of the products shown in Figure 3. The latter also shows some of the oxidative cleavage that results from autoxidation from other unsaturated esters. These cleavage products impart odor and flavor to oils and must be removed by steam

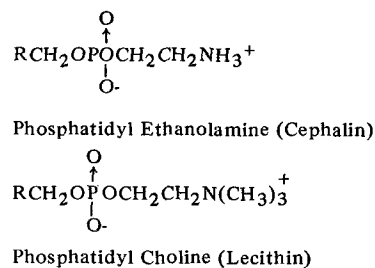


FIG. 1. Two phospholipids, ionic part only.

TABLE I  
Hydrated Ions

Hydrogen	Metals
H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	Na(H <sub>2</sub> O) <sub>4</sub> <sup>+</sup>
H <sub>5</sub> O <sub>2</sub> <sup>+</sup>	K(H <sub>2</sub> O) <sub>4</sub> <sup>+</sup>
H <sub>7</sub> O <sub>3</sub> <sup>+</sup>	Fe(H <sub>2</sub> O) <sub>6</sub>
H <sub>9</sub> O <sub>4</sub> <sup>+</sup>	Mg(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>
	Ni(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>

deodorization. At high temperatures, the hydroperoxides are also destroyed.

### CENTRIFUGATION

The basic theory for centrifugation is outlined in formulas C1-C11 below.

$$F = ma \quad (C1) \quad F = w^2r(C2)$$

$$F = (M'-m)w^2r(C3) \quad F = \text{Force}$$

m' = mass of the particle

m = mass of equal volume of liquid

w = angular velocity

r = radial distance

$$F = \Delta\rho \frac{\Pi}{6} D^3 w^2 r \quad (C4) \quad \text{where}$$

$\Delta\rho$  = difference in density between particle and liquid

$$F' = 3\Pi\eta Dv(\text{Stokes Law}) \quad (C5)$$

$\eta$  = viscosity of liquid

v = speed of particle

D = diameter of particle

$$\Delta\rho \frac{\Pi}{6} D^3 w^2 r = 3\Pi D v_s$$

$$v_s = \frac{\Delta\rho D^2 w^2 r}{18 \eta} \quad (C6)$$

$$v_g = \frac{\Delta\rho D^2 g}{18 \eta} \quad \text{gravity} \quad (C7)$$

$$x = v_s t = \frac{\Delta\rho D^2 w^2 r}{18 \eta} \cdot \frac{V}{Q} \quad (C8)$$

t = time      V = volume of liquid  
Q = volume rate of flow

when x = s/2 (cutoff)

$$Q = \frac{\Delta\rho D^2}{9\eta} \cdot \frac{V w^2 r}{s} \quad (C9)$$

$$Q = 2 v_g \Sigma \quad (C10)$$

$$\Sigma = \frac{V w^2 r_o}{g s_o} \quad (C11)$$

r<sub>o</sub> = effective radius

s<sub>o</sub> = settling distance

Σ = Index-centrifuge size

With any moving particle, the force (F) is equal to the mass times acceleration, C1. In a centrifuge, that force is the square of the angular velocity (w) times the radius, C2. In liquid media, force is equal to the difference between the mass of the particle and the mass of an equal volume of the liquid media (see C3). For spherical particle, the equation becomes C4. Here  $\Delta\rho$  is the difference in density and  $\Pi D^3/6$  is the volume of the spherical particle.

The force that opposes the removal of this particle or sedimentation by Stokes Law is equation C5, where  $\eta$  is viscosity of liquid and v is the speed of the particle. If we

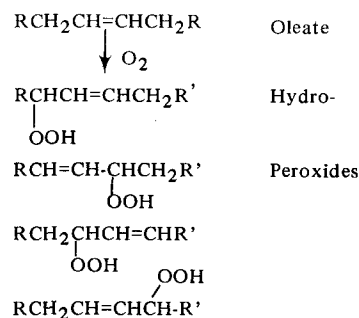


FIG. 2. Autoxidation of oleic ester.

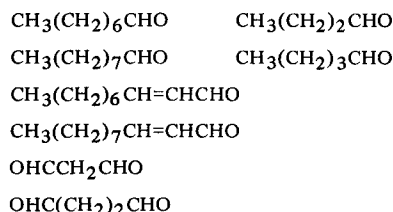


FIG. 3. Cleavage products.

equate these two equations and solve for the settling speed  $v_s$ , we have equation C6. The velocity ( $v_g$ ), the settling speed in a settling tank due to gravity, will be equation C7, where g is gravity and replaces  $w^2r$ .

If we assume a centrifuge bowl in the shape of a cylinder with liquid fed continuously into one end and out the other, the liquid will be against the wall with a thickness, S. The time, T, during which the liquid is in the bowl is V/Q, where V is the volume in the bowl and Q is volume rate of flow. When the thickness is small, the distance x settled by the particle becomes C8, where  $v_s$  comes from formula C6 and V/Q is equal to t as shown in C8.

Half of the particles of diameter D will be sedimented and half will not be when x = S/2. This is known as 50% cut-off or simply cutoff. The flow Q then becomes formula C9. The first half of this equation follows Stokes Law, and the second follows the parameters of the rotor involved. Thus, Q is proportional to 2 times the  $v_g$  times Σ, which is the summation of the parameters of the rotor expressed in formula C11.

### BLEACHING

The removal of the effect of pigments can be carried out in several ways:

1. Adsorption of pigments by clay, carbon black, or other suitable material
2. Heating the oil particularly in the presence of oxygen or hydroperoxides that may have been formed by previous exposure of the oil to air
3. Heating in the absence of air.

Natural or activated clays are most generally used for adsorption of carotenoid and chlorophyll pigments. Freundlich's theory appears to apply to this physical separation. Pigments are adsorbed in multilayers on clay particles that have been activated naturally or artificially with acid. Freundlich's equation is

$$\frac{X}{m} = Kc^n$$

where X is the amount of substance adsorbed, m is the amount of adsorbent, c is the amount of residual material, and K and n are constants inherent in the system. Acid activated clays are generally used for harder-to-bleach oils. Activation is believed to proceed by replacing aluminum ions in the clay structure as shown in Figure 4. A dried clay

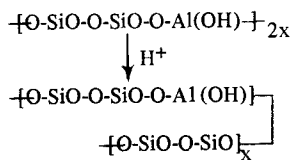


FIG. 4. Clay activation.

from which all the water is removed is less effective than a clay containing adsorbed water. However, best results are obtained when the clay is added at an oil temperature below the boiling point of water, then heated to remove water that may be absorbed in the clay lattices.

### DEODORIZATION

This operation, sometimes known as vacuum steam distillation, is designed to remove all oxidative cleavage products that impart an odor or flavor to the oil. It may also remove tocopherols, sterols, and other useful minor constituents or other undesirable foreign material. It will also remove substantial amounts of free fatty acids and lower them to 0.02-0.05%. The theoretical considerations that apply to this operation are primarily Raoult's and Dalton's laws: Formulas D1-D4 shown below. In D1, or

$$D1 \quad \rho_v = P_v \frac{V}{O+V} \quad \text{Raoult's Law}$$

Since V is small compared to O

$$D2 \quad \rho_v = P_v \frac{V}{O}$$

$\rho_v$  = equil. pressure of volatiles

$P_v$  = vapor pressure of volatiles

V = moles of volatiles

O = moles of oil

$$D3 \quad \frac{dS}{dV} = \frac{\rho_s}{\rho_v} \quad \text{Dalton's Law}$$

S = moles of steam, V = moles of volatiles,

$\rho_s$  = partial pressure of steam,  $\rho'_v$  = partial pressure of volatiles

Since  $\rho'_v$  is small compared to  $\rho_s$  and  $\rho_s \approx P$ ; D-3 becomes

$$D4 \quad \frac{dS}{dV} = \frac{P}{\rho'_v} \quad (P = \rho'_v + \rho_s)$$

$$D5 \quad S = \frac{PO}{EP_v} \left( \log \frac{V_1}{V_2} \right)$$

Raoult's Law, as applied to volatiles in an oil, the moles V of volatiles is small compared to O, the moles of oil, so that D1 can be expressed as D2. Dalton's Law, which applies to the steam distillation, can be expressed as D3. Since  $\rho'_v$  is small compared to the partial pressure of steam  $\rho_s$ , equation D3 becomes equation D4. Equations 2 and 4 can be further employed by use of efficiency (F) equaling the partial pressure of the volatile substance divided by the equilibrium pressure of the volatile component. Thus, we can solve for S to obtain D5, where E is the efficiency and  $V_1$  is initial and  $V_2$  is the final concentration of volatile substance in the oil. Therefore, the steam requirements are proportional to O, the amount oil, and P, the absolute pressure on the system, and inversely proportional to the vapor pressure of the volatile component  $P_v$ . Other and practical considerations are left to other authors in this symposium.

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