WINTERIZATION

In edible oil processing, a fractionation process consists of a controlled cooling of the oil, thereby inducing a partial, or ‘fractional’, crystallization. The remaining liquid is then separated from the solid fraction by means of a filtration or centrifugation.

The descriptive term of winterization evolved from the observation that refined cottonseed oil stored in outside tanks during the winter months physically separated into a hard and clear fraction. Topping or decanting the clear oil from the top of the tanks provided oil that remained liquid without clouding for long periods at cool temperatures. In fact, some cottonseed salad oils routinely had cold test results of 100 hours or more when topped from outside storage tanks. The clear oil portion became known as winterized salad oil. The hard fraction from the bottom of the tanks was identified as stearin, which is the solid portion of any fat. A need for a liquid oil with these characteristics was created by the use of refrigerators in the home and the requirements of the mayonnaise and salad dressing industry. Mayonnaise could not be made from oils that would crystallize in the refrigerator and cause the emulsion to break. New terminology emerged because of this association with mayonnaise. Winterized oil became known as salad oil. Summer oils, or oils that had not been subjected to winterization, became known as cooking oils. As the demand for salad oils increased, it became impossible to rely on long-term storage of refined oils for the winterized oil requirement. Processors recognized the obvious solution and created winter conditions indoors.

This kind of fractionation process has been applied for almost 150 years. In most literature, Hippolyte Mège-Mouriès is credited with the invention of “a patented method to produce certain fats of animal origin”. In fact, he concocted the production of a sort of margarine fat, by separating a liquid fraction from ordinary tallow after gentle cooling. But with only temperature difference as the driving force, a fractional crystallization of a fat is a perfectly natural, spontaneous phenomenon. So it was also observed that in palm (kernel) oil harvested in tropical regions, small crystals would appear upon cooling and form a crystal suspension in the wooden barrels during shipping to chillier Western Europe. These slightly denser solids eventually settled, and such fractions could effectively replace hardened fats in

margarines . In a more evocative twist, we could therefore consider these wooden shipping drums the very first oil crystallizers, with just the peaceful ocean waves providing the necessary agitation to keep the mix in suspension. Moreover, the natural fractional crystallization of fats when mildly cooled is echoed in the term ‘winterization’, referring to the habit of leaving large oil tanks quiescent in wintertime to induce some mild crystallization and obtain a liquid fraction with improved cold stability, in an economic fashion.

fractionation technologies:

Actually only two main fractionation technologies are used in the 21st century’s edible oil industry:

- Dry fractionation, also known as crystallization from the melt, is fractional crystallization in its most simple form, and the economy of the technology allows it to be used for production of commodity fats. Dry fractionation has long been regarded as an unpredictable, tedious and labor-intensive process. However, the relatively cheap dry fractionation technique has evolved to the modification technology of the 21st century , as without additives, polluting effluents or post-refining involved, the sustainability and safety of the process are second to none.

- Solvent fractionation, already patented in the 1950s, involves the use of hexane or acetone to let the high-melting components crystallize in a very low-viscosity organic solvent. This can be helpful with respect to the selectivity of the reaction, but mainly offers advantages in the field of phase separation: Much purer solid fractions can be obtained, even with a vacuum filtration. Being a more expensive process, it is less common than dry fractionation and only comes into the picture when a very high added value of (at least one of) the resulting fractions makes up for the high cost.

Classical Winterization Process

- The indoor process developed to simulate the natural winter process consisted of a chilled room held at 42°F (5.6°C) with deep, narrow, rectangular tanks to provide the maximum surface exposure to cooling.

- Warm, dry, refined, and bleached oil pumped into the chill room tanks began to cool and crystallize-out stearin immediately, but slowly. Convection heat transfer simulated the outside storage conditions.
- Agitation was avoided because it fractured the crystal, causing formation of small, soft crystals that were difficult to filter.
- Cooling with a 42°F room temperature simulated winter conditions in the southern United States closely and required two to three days to produce the desired large crystals for filtering.

After the oil temperature equated with the room temperature, it was held for several hours to allow the stearin or hard fraction to precipitate more fully.

The stearin was separated from the liquid oil by filtering with plate and frame presses.

Early installations relied on gravity feed to the presses, but later compressed air or positive displacement pumps were utilized to exert a pressure of 5 to 20 psig to increase the filtration rate. Care was exercised to avoid breaking up the crystals excessively.

- A slow filtration rate was necessary because of the high oil viscosity and excessive pressure pressed the stearin into the filter cloths, causing a blockage that stopped the oil flow.

  A large filter area on the order of 2 to 3 pounds of oil per hour per square foot was the general guideline.

  The stearin cake was melted with hot fat for removal after the filter press was full.
- Winterization is still performed using the classic techniques outlined above, but many processors have made equipment and process modifications to improve efficiency.

  Jacketed-enclosed tanks equipped with programmable cooling and agitation have evolved as crystallization cells to replace the open-top, narrow, rectangular tanks cooled by the chill room temperature. However, attempting to force crystallization by means of an excessively cold coolant and rapid agitation results in small crystals that are virtually unfilterable. Recessed plate and frame or pressure leaf filters have been used in winterization because these filters have the cake-holding capacity that the process requires. Obviously, when 15% or more of the feed is removed in the form of stearin, a substantial solids retention capacity is needed.

Separation of the stearin from the liquid oil by means of a centrifuge has had some success. The main problem encountered with centrifugal separation is liquid oil yield, as the stearin tends to trap excessive amounts of oil.

Winterization Principle

Winterization is a thermomechanical separation process where component triglycerides of fats and oils are crystallized from a melt. The two-component fractional crystallization is accomplished with partial solidification and separation of the higher melting triglyceride components. The complex triglycerides may have one, two, or all three fatty acids, either all the same or different in any of the possible configurations depending on the source oil and prior processing. Fat crystallization occurs in two steps:

1. Nucleation
2. Crystal growth.

The rate of nucleation depends on the triglyceride composition of the oil being winterized, the cooling rate of the oil, the temperature of the nucleation, and the mechanical power input or agitation.

Growth rate is dependent on the crystallization temperature, time, and mechanical input or agitation.

A careful selection of the process variables for a particular oil is very important. The ideal is to produce a small number of nuclei around which the crystals grow larger in size with cooling. A large mass of small crystals that is difficult to filter results when a large number of nuclei are formed.

Poor separation and yield also result when crystals group together in clumps that trap large quantities of the liquid phase. The effect of the major processing variables upon winterization performance is discussed below.

Source Oil Composition

Nucleation and crystal growth depend on the composition of the oil being winterized. The various triglycerides in a particular oil will fractionate in the following order

: (1) Trisaturate, S3

(2) Disaturate monounsaturate, S2U

(3) Monosaturate diunsaturate, SU2

(4) Triunsaturate, U3.

A portion of the higher melting glycerides will be found with the lower melting liquid oils as a result of eutectic formation and equilibrium solubility. Because the mixture of triglycerides in an oil is too complex to predict its phase behavior, a given set of winterization conditions is applicable only for the particular feed oil.

Cooling Rate

An essential requirement of the winterization process is a slow rate of chilling. Rapid cooling of the oil results in;

(1) a mass of very small α-crystals

(2) a high nucleation rate that increases the viscosity, which, in turn, restricts crystal growth.

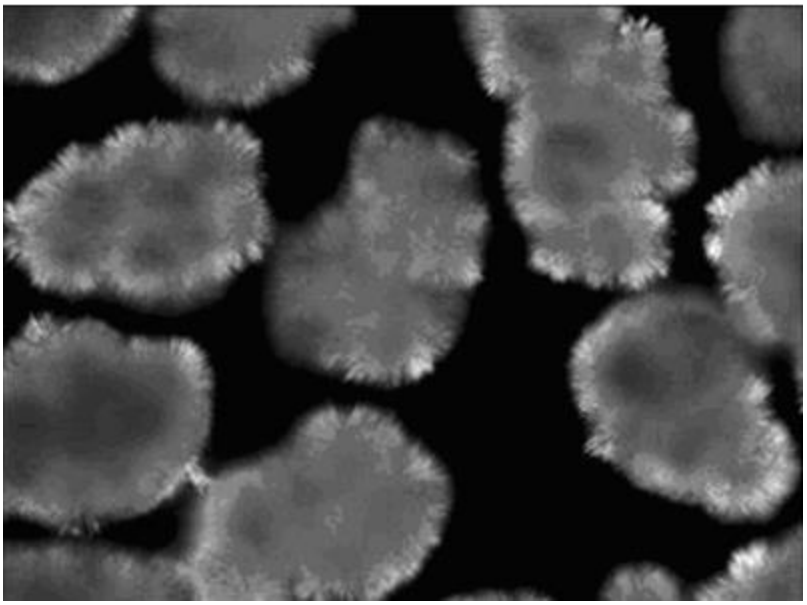
Slow controlled cooling rates produce stable β- or β′-crystals depending on the dominant crystal habit for the source oil winterized, and the viscosity remains low enough to permit nuclei movement to allow crystal growth. Therefore, the cooling rate is dependent on the source oil and prior processing.

Crystallization Temperature

The crystal growth rate is affected by the temperature of crystallization. A high viscosity resulting from too low a temperature reduces the crystal growth rate. Control of the temperature after crystallization begins is important for transformation from the α to the stable β′- or β-crystal habit.

If the process is not properly controlled at this stage, an unstable crystal will develop. A temperature differential between the coolant and the oil must be maintained to avoid shock chilling. A 25°F (14°C) differential has been found appropriate for oil at the beginning of the process. The differential can be reduced to 10°F (5.6°C) by the time the oil reaches 45°F (7.2°C). If the coolant is allowed to become too cold in relation to the oil, a heavy layer of stearin will build up on the surfaces and insulate the oil from the coolant.

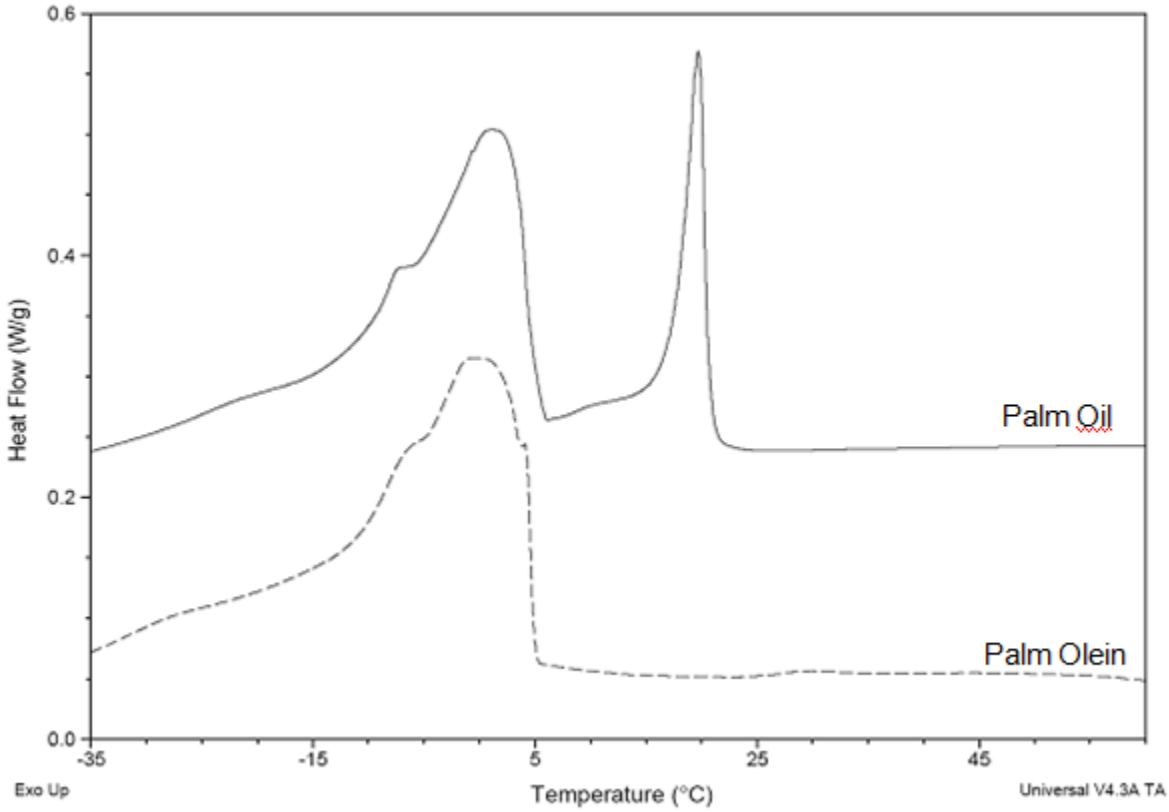
If the crystal growth is well controlled, the crystal aggregates result in sharply discrete and dense spherulitic structures, sometimes measuring up to several millimeters in diameter, which are fairly uniform in size and shape (Fig. 1).



Polarized light microscopic picture of typical spherulitic crystals developing in palm oil fractions.

Note that such gentle cooling means in fact imposing very low supercooling conditions, and it will result in a formation of fewer and larger crystals, because the said conditions simply rule out the existence of a mass of tiny crystals. Fat crystallization is a fairly exothermic reaction (up to 180 kJ can be released for every kg of crystals formed), so the efficiency with which this energy can be removed is an important design feature. For most industrial crystallizers, this ranges between 120 and 200 $W/m^2 \cdot K$.

In order to preserve the selectivity and to avoid the temperature gradients within the melt, the cooling rate under crystallization conditions is quite slow (0.2-3°C/h), depending on the sensitivity of the reaction and the performance of the crystallizer. Sensitivity of the reaction might be a little of a subjective term, but it can be quite elegantly illustrated by Figure . This shows a differential scanning calorimetry profile of palm oil (full line above) and palm olein (dotted line below).



DSC cooling profile (-5°C/min) of palm oil and its derived palm olein fraction. Exothermal peaks are shown upwards.

The upward peaks in the profile show at which temperatures and how much heat of crystallization will be released upon cooling (here at 5°C/min!). For palm oil, the sharp peak on the right is created by the fast solidification of predominantly trisaturated triglycerides. It is largely (and not solely, as some intersolubility will inevitably occur) this fraction that is crystallized in the first step or 'cut' in multistage palm oil fractionation.

Agitation Rate

Crystal formation is hastened by stirring to bring the first crystals into contact with more of the liquid; however, mild agitation rates are recommended because high shear rates fragment the crystal during the growth stage, thus producing smaller crystals instead of the desirable large crystal.

Crystallization Time

Crystallization is inseparably linked to two elements of time:

(1) the time it takes to lower the temperature of the material to the point where crystallization will occur

(2) the time for the crystal to become fully grown.

The rate of cooling is a primary factor for determining the size, amount, and stability of the crystals formed. In general, crystals assume their most highly developed and characteristic forms when grown slowly from a melt or solution only slightly supercooled, in which the liquid freely circulates around the crystal. A typical time–temperature sequence for winterization of cottonseed oil is;

1. Refined and bleached cottonseed oil is transferred to the chilling units at 70 to 89°F (21.1 to 26.7°C).
2. The oil is cooled to 55°F (12.8°C) in 6 to 12 hours, when the first crystals usually appear.
3. The oil is cooled to 45°F (7.2°C) in 12 to 18 hours with a reduced cooling rate. At this point, a 34 to 36°F (1.1 to 2.2°C) heat of crystallization temperature increase should be observed.
4. After the oil temperature drops slightly below the previous low, approximately 42°F (5.6°C), it is maintained at this temperature for approximately 12 hours. This period is critical for the effectiveness of the process. Because the oil is viscous and molecular movement is slow, crystals continue to grow after the minimum temperature is reached.

The Separation Stage

Although the triglyceride separation theoretically is already established during crystallization, it is clear that the separation stage itself effectively determines the product yields as well as the stearin quality. As more residual olein can be expelled from the solids cake, the final stearin will be more concentrated in crystals and will turn out ‘purer’ and will display higher and steeper melting. The olein quality is determined entirely by the amount and selectivity of crystallization in the preceding stage. In some applications, the formed crystals are often not sufficiently stress-resistant and get squeezed through the filter medium. Obviously, such contamination of crystals in the olein phase affects the efficiency of the fractionation process negatively and results in a liquid phase with inferior cold-stable properties. Overall,

the ‘permitted’ degree of olein dilution in the stearin cake determines the choice for the applied separation technology, exemplified in Table

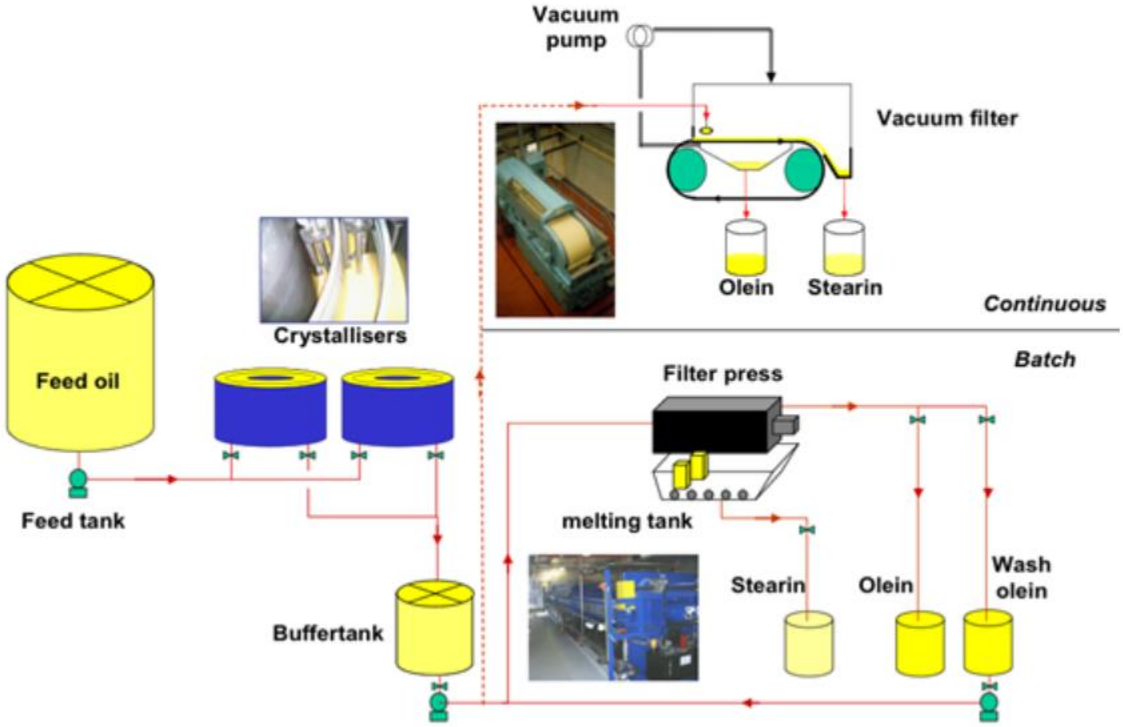
Table 1. Different separation systems for palm oil fractionation [6]

	Vacuum filtration	Centrifugal nozzles	Membrane press (16 barg)
IV Palm oil	52	52	52
IV Palm olein	56-57	56-57	56-57
IV Palm stearin	40-42	36	30-32
Solids in cake (%)	46	-	65
Olein yield (%)	72	76	82

Membrane press filtration, as also used in for example sludge dewatering systems, is by far the most used separation technology in dry fractionation nowadays. Such filters consist of a large steel frames that can easily hold up to 150 filter plates together, each plate counting for up to 7 m^2 of filtration surface and over 100 L filter chamber volume.

The Fractionation Plant Assembly

Figure presents a general layout of a present-day dry fractionation process. Often multiple crystallizers are used in (overlapping) series. This is not only a matter of capacity, it is also in order to maximize the use of the filter; by a good planning of the crystallization times of filtration, the expensive (batch) filter should be in constant operation.



Layout of a typical dry fractionation process.

The reduction of dead time of a filter can also be established by means of a crystallized offer buffer tank; each crystallizer can be quickly drained and made ready to receive the next batch of oil, while the cooled buffer tank will send set volumes of crystal slurry to the filter, whenever it is ready. Continuous filtration systems have been a very elegant strategy in dry fractionation as well, although currently, the demand for purer solid fractions as obtained by filter chamber compaction has pushed continuous belt filters somewhat out of the dry fractionation market.

It should be kept in mind that fractional crystallization of a triglyceride oil is a relatively slow process and is therefore the time-determining stage; some simple fractionations can be established in about 5 hr crystallizer residence time, whereas more complex oils can require up to 3 days of cooling and crystal maturation before being sent to the filter.

Solvent Winterization

Salad oil production with the traditional winterization procedure is a slow process. Two to three day chilling time is required for good filtration and yield. Most vegetable oils that cloud at refrigerator temperatures can be solvent winterized for

better yields and to produce a salad oil of better quality in less time than by the conventional process. Comparison of the two procedures indicates many similarities. The major advantage of a solvent winterization system include:

(1) viscosity is considerably lower, which allows a faster crystal growth for more rapid stearin separation;

(2) the salad oil produced has a better resistance to clouding at cool temperatures for longer cold tests;

(3) less liquid oil trapped in the stearin component for higher salad oil yields.

An operational continuous solvent process was described by Cavanagh and later by Neumunz for winterization of cottonseed oil. Miscella containing 30 to 60% by weight of oil in hexane with a 50% solution preferred is cooled rapidly with a heat exchanger to either 20 to 26°F (–6.6 to –3.3°C) or 8 to 12°F (–13.3 to –11.1°C).

After cooling, the miscella passes through a continuous winterizing column, which cools with a series of agitated trays over a 40- to 60-minute period to temperatures as low as –4°F (–20°C). A continuous solids discharge centrifuge separates the solid stearin from the liquid miscella. The solvent is removed from the liquid oil portion with an evaporator system before deodorization. The solid discharge from the centrifuge is filtered to remove any foreign material before the residual 10 to 15% hexane solvent is removed with an evaporator system. Controlled agitation of 1 to 10 rpm and a controlled temperature drop to 0°F produces harder, firmer, more compact stearin crystals in solvent, and less oil is entrapped than with conventional winterization systems. Table 2.6 provides a comparison of cottonseed salad oil stearin analytical characteristics from a conventional process and a solvent process.

Cottonseed Salad Oil Stearin Analysis

Winterization Process	Conventional	Solvent
Iodine value	95.5	71.6
Solids fat index		
50°F/10.0°C	21.6	52.3
70°F/21.1°C	1.3	33.7
80°F/26.7°C	—	1.2
92°F/33.3°C	—	0.1
Fatty acid composition, %		
C-14:0 Myristic	0.7	0.6
C-16:0 Palmitic	34.6	52.1
C-16:1 Palmitoleic	0.6	0.8
C-18:0 Stearic	2.1	1.9
C-18:1 Oleic	15.8	9.1
C-18:2 Linoleic	46.2	35.5

Winterization Process Control Procedures

The acceptability of winterized oil is almost always determined by cold-test analysis. This method measures the ability of the oil to resist crystallization. The cold-test result is the number of hours at 32°F (0°C) required for an oil to become cloudy. AOCS Method Cc 11-53 indicates that an oil has passed the test if it is clear and free of any cloud at 5.5 hours, however, most processors and customers have more stringent requirements for cold-test hours. Cottonseed and soybean winterized oil products normally have a minimum cold-test limit of 10 hours and some are as high as 20 hours for special products.

Processors have investigated many different potential process control evaluations, procedures, and methods to be determine that the winterization process is in control on a timely basis; however, cold test is still the most definitive evaluation, even though the results are not available until a lengthy period after the oil has been winterized. Usually, the winterized oil production is segregated in separate tanks until the cold-test results are available. If the oil fails to meet the specific number of hours, it must be rewinterized. Oils that meet the requirements are transferred to salad oil storage for subsequent deodorization, packaging, or shipment as required. This after the-fact analysis to determine the acceptability of

the winterized oil places more emphasis on process control techniques to ensure that all of the best practices are continually observed.

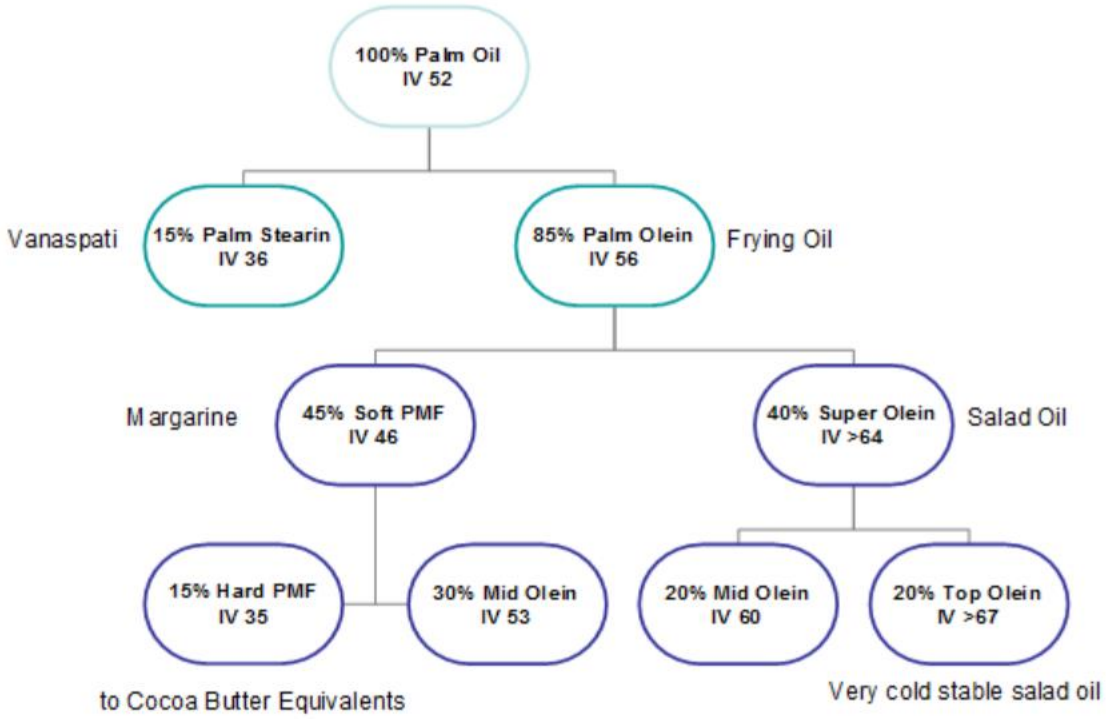
Winterization Applications

Historically, winterization has always been associated with cottonseed oil. It and other liquid oils that contain fractions that solidify when chilled must be winterized or fractionated to remain clear at cool temperatures. Oil that is to be refrigerated or stored in cool warehouses must resist clouding for a period of time to be acceptable aesthetically or for performance. Winterized cottonseed oil was the standard salad oil used by retail-trade food processors to produce mayonnaise and other salad dressing products because of its pleasing flavor and flavor stability.

Soybean oil was rejected as a salad oil both at the retail level and by food processors until the flavor stability problem was remedied with partial hydrogenation to reduce the linolenic (C-18:3) fatty acid content. Hydrogenation to improve flavor stability also produced a hard fraction in the soybean oil, which crystallized at cool temperatures similar to cottonseed oil. Winterization was employed to separate the hard and liquid fractions. Supply-and-demand economics and performance elevated partially hydrogenated winterized soybean oil to the leading winterized salad oil product in the United States.

A comparison of the two winterized oil products is presented in Table Winterization of hydrogenated soybean oil is very similar to that of cottonseed oil except that less time is required for crystallization and filtration. The inherent crystallization tendencies for the two source oils are different; the stable crystal form for soybean oil is β, but it is β′ for cottonseed oil. β-crystals are large, coarse, and self-occluding, whereas the β′-crystals are small, needle-shaped crystals that pack together to form dense, fine structures. Typical Cottonseed Oil and Partially Hydrogenated Soybean Oil Winterized Salad Oil Components

In essence, the goal of fractionation is to create the biggest possible difference between two fractions. Palm oil is by far the most fractionated oil in the world. Given the broad spectrum of triglycerides and also its naturally high amount of palmitic acid that gives a fat ‘body’ at room temperature, the separation of palm oil into sharply defined fractions usually happens in a multi-stage process



Multistage fractionation of palm oil with possible food applications for the various fractions.

The first step of dry fractionation of palm oil yields olein fractions with a cloud point below 10°C. The olein fractions are used as a substitute for soft oils in frying, cooking and salad oils or are being further fractionated. Together with a further development of single-stage palm oil fractionation by technological improvements, there is an increased tendency to execute a double or triple fractionation of palm oil in order to produce fractions with specific characteristics such as high IV superoleins (IV > 65) and hard palm-mid-fractions (hard PMF) (IV < 36).

The latter fraction can serve as a feedstock for the production of typical cocoa butter equivalents (CBE), which are non-lauric fats similar in their physical and chemical properties to cocoa butter. They are often prepared by solvent fractionation [7], though the more contemporary developments within dry fractionation (better suited crystallizers, improved separation technologies) are closing the gap between the quality of solvent- and dry-fractionated hard PMF.

Another technological field of interest is the use of plug flow reactors that allow the fractional crystallization in a continuous fashion, offering considerable reduction in operation costs (such as steam usage and cooling power). Indeed, just as in any other edible oil processing technology, there is a continuous quest for economization and

process optimization. Heat recovery systems, crystal seeding installations, optimized mixing procedures and elegant plant layouts can all contribute to maximize capacity and minimize costs for a dry fractionation plant.

One final comment is that the process technologist should always remember that a fractionation process yields two products, and thus that the sum of the value of the two fractions should always exceed the processing cost and feedstock cost. This is why the feasibility of multistage fractionation is not only a matter of technological know-how, but also a matter of having markets for all 'by-products' generated along the way.

Source Oil	Cottonseed Oil			Hydrogenated Soybean Oil		
Winterized Oil Component	Whole Oil	Salad Oil	Stearine	Base Stock	Salad Oil	Stearine
Fraction, %	100.0	84.6	15.4	100.0	82.9	17.1
Iodine value	109.0	113.5	90.6	108.7	111.4	95.7
Fatty acid composition, %						
C-14:0 Myristic	0.9	0.9	0.7	—	—	—
C-16:0 Palmitic	24.8	21.3	38.2	11.2	10.2	15.0
C-16:1 Palmitoleic	0.5	0.5	0.3	—	—	—
C-18:0 Stearic	2.6	2.6	2.3	4.8	4.1	7.9
C-18:1 Oleic	16.9	16.9	13.8	45.4	45.2	46.0
C-18:2 Linoleic	53.7	53.7	44.2	35.4	37.5	29.1
C-18:3 Linolenic	0.2	0.2	0.1	3.0	2.8	1.9
C-20:0 Arachidic	0.2	0.2	0.2	—	—	—
Cold test, hours	none	24.0	none	none	10.5	none