

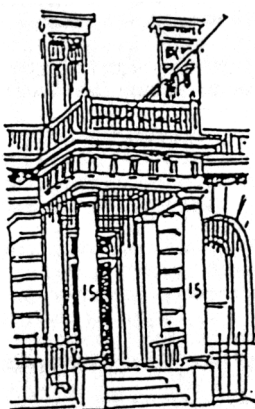
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DEVELOPMENTS IN FAT FRACTIONATION TECHNOLOGY

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Developments in Fractionation Technology

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Abstract

Among the various modification processes used in the oils and fats industry, fractionation has gained increasing interest. More than others, the dry fractionation process offers interesting perspectives to a whole variety of fatty matters, as it is a pure physical and fully reversible process. Today, the technique is already applied on a large scale in the palm oil and milk fat industry.

The ever increasing demand for products with very specific physical properties, has called for new developments in fractionation. Multifunctionality and flexibility are becoming very important as more and more fatty matters of different origins are fractionated.

The present paper describes some basic principles of fractionation and the main features to which today's fractionation plants have to respond. Some new developments in fractionation as well as the increasing interest in understanding the fractionation process from a more scientific standpoint are reviewed in detail.

Introduction

The applicability of oils and fats is strongly related to their physical characteristics. Due to their specific chemical composition, oils and fats exhibit a different aggregation state at ambient temperature. Depending on their physical state, the oils and fats can be divided into two major categories, the so called soft and hard oils.

The soft oils, as for example soy bean oil, are fully liquid at ambient temperature due to their high degree of unsaturation. In order to widen their use in more solid state applications, these oils are partially hydrogenated and/or interesterified in order to change their physical behaviour. On the other hand, the so called hard oils, as for example palm oil, are semisolid at ambient temperature, which restricts their use in a whole variety of products where liquid oils are preferred. In order to increase their range of application, they are fractionated to separate the liquid fraction from the solid portion.

Hydrogenation, as well as interesterification, are basically chemical and hence irreversible processes. Hydrogenation is normally applied to increase the hardness of the oil and to some extent also to improve its oxidative stability. Interesterification produces changes in the physical characteristics by rearranging the fatty acid distribution. Due to the contaminative effect of these catalytic reactions as well as to the side-reactions which cannot be fully excluded, the chemical processes always imply a refining step in order to make the modified oil edible again.

The fractionation process, on the other hand, is a pure physical and fully reversible modification process. Especially the dry fractionation technique is the most interesting alternative as it implies no contamination at all. Today, fractionation is applied more and more to extend the use of a whole variety of fatty matters as well as to replace fully or partially the chemical modification processes.

Fractionation principle

Fractionation can be generally defined as a thermomechanical process in which a multicomponent mixture is physically separated into two or more fractions with distinct physical and chemical properties.

The separation can be based on either a difference in crystallization, solubility or evaporation of the different components. In most cases, however, the term fractionation refers to the separation process where part of a fatty matter, usually an oil or a fat, is crystallized in a selective way, after which the remaining liquid phase is separated from the solid one by means of filtration or centrifugation. Crystallization can take place either in the melt or in a diluted solution.

Fractionation systems

The fractionation technology, although already applied industrially for several decennia, still remains somewhat unknown and underestimated. This is to a large extent due to the very complex nature of the process itself. Over the years, several systems have been developed (table 1). There are generally three different fractionation principles: dry fractionation, solvent fractionation and detergent fractionation. The first system implies no additives at all, whereas the latter systems involve the use of a solvent or a detergent to improve separation efficiency.

Solvent fractionation

In solvent fractionation, crystallization is performed in diluted solutions using mainly acetone or hexane as solvent, thereby reducing the viscosity. The process is characterized by a short crystallization time and easy filterability. The main advantage of solvent fractionation is the high separation efficiency and hence improved yield, which results in a higher purity of the finished products. The reason for this can be explained quite simply by the fact that with any type of separation technique, it is not possible to remove all liquid from the solid portion. Part of the liquid always remains entrapped within the solid phase. The amount of liquid is strongly dependent on the origin of the fatty matter as well as on the crystallization conditions and the separation technique being applied. In a diluted solution, as is the case in solvent fractionation, this liquid portion consists of a considerable quantity of solvent which, after separation, is evaporated, leaving behind a much lower quantity of liquid oil in the solid phase.

Due to the high production costs and capital investments, as well as the risks, solvent fractionation is becoming less interesting. Today, most of the plants in operation, produce speciality fats as for example cocoa butter replacement fats.

Detergent fractionation

Detergent fractionation was developed to ease the separation of the crystallized phase from the remaining liquid by adding an aqueous detergent solution to the crystallized oil. The wetting agent, usually sodium lauryl sulphate, in combination with an electrolyte, usually magnesium sulphate, allows the crystals to be easily suspended in the aqueous phase. The separation of the water phase from the remaining liquid oil is done by centrifugation. The water phase is subsequently heated and the melted stearin is recovered in a second centrifugation step.

After separation, the olein and stearin fractions are washed and dried in order to remove traces of detergent.

Today, the technique has lost its interest due to the high costs and the contamination.

Dry fractionation

This is the simplest and by far the cheapest separation technique as it involves no supplementary posttreatment of the finished products. The oil as such is partially crystallized

by cooling the melt in a controlled manner to the desired end temperature, after which the remaining liquid is filtered in a vacuum or membrane press filter.

Due to the continuous development of the dry fractionation process, more and more fatty matters of different origin are or can be fractionated with a high degree of selectivity. This has made especially detergent fractionation superfluous. A whole variety of products, normally produced by solvent fractionation, can also be obtained by dry fractionation.

Some products, as for example palm kernel oil, are fractionated in a special way: here, the oil is solidified into cakes which are then wrapped into filter cloths and subsequently squeezed in a hydraulic press operating at very high pressures (>100 bars). This process can also be classified as a dry fractionation technique. Today the technique is gradually modified by replacing the labour intensive hydraulic presses by high pressure membrane press filters.

Apart from the above mentioned fractionation processes, the dewaxing and winterization processes are also basically dry fractionation processes. Due to the very small amount of solids to be removed (less than 5%), these processes are regarded more as a refining process rather than a modification process and will therefore not be further discussed here.

Beside the fractionation techniques which are grounded on a difference in solubility of the different components in the solid state, some other techniques are practised or are under investigation in the oils and fats industry, based on others physical principles.

Distillation

Fractional distillation is based on a difference in evaporation temperature (boiling point) of the different components. The principle cannot be applied to glycerides as these products decompose before they vaporize. The technique, however, is applied on a large scale in the oleochemical industry to fractionate fatty acids according to their chain length. The most important aspects of fatty acid distillation are the production of high quality products with excellent color and low impurity levels. Due to the thermal instability of fatty acids, distillation is normally performed under vacuum and in specially designed packed columns to reduce temperature and product hold-up.

Supercritical fat extraction

The separation of triglycerides by means of supercritical extraction, is based on their solubility in the supercritical fluid, usually carbon dioxide, which is in turn a function of the fatty acid chain length. Experiments have proven that it is possible to separate for example milk fat into fractions rich in short-chain, medium-chain and long-chain triglycerides.

There is up to now no industrial application for this type of fractionation, due to the very high costs and the technical complexity. Especially the very high pressures required for this type of extraction hamper its application on a large scale.

Table 1: Different fractionation processes used in the oils and fats industry

Fractionation processes	principle
Dry fractionation: - fractionation - hydraulic pressing - (winterization) - (dewaxing)	crystallization
Solvent fractionation (hexane/acetone)	
Detergent fractionation (aqueous)	
Fractional distillation	volatility
Supercritical extraction	solubility

Dry fractionation Process

A whole variety of fatty matters are already dry fractionated (table 2). Best known are palm and palm kernel oil, hydrogenated soybean oil, tallow and milk fat. Most of the fatty matters are refined and chemically modified before they are fractionated.

Some products cannot be obtained in a single fractionation step, but require several subsequent fractionations.

The dry fractionation process principally consists of two steps, crystallization and separation.

1. Crystallization

The crystallization process of oils and fats is quite complex due to the existence of multiple polymorphic forms (α , β' , β) and the intersolubility behaviour of the different components in the solid state: depending on the crystal form as well as on the composition, the different triglycerides may cocrystallize to form mixed crystals.

The α , β' and β crystal forms are of increasing stability in that order. Furthermore, the rate of crystallization of the α form is greater than that of the β' form, which in turn is greater than the β polymorph (table 3).

Different thermal conditions are needed to induce crystallization of the different polymorphic forms. If supercooling is carried out too rapidly, α -crystallization occurs, yielding a dense mass of very small crystals. The β form, on the other hand, is very difficult to obtain and only appears in some exceptional cases, as for example in

cocoa butter. The β -crystal texture does not always allow easy separation and is therefore to be avoided in most cases. In order to obtain good separation, the crystals should be firm and of uniform spherical size, which is a condition found when they are mainly in the β' form.

Table 2: Application field of dry fractionation in oils and fats industry

Dry Fractionation --> single stage --> multi stage	
Vegetable oils	Animal fats
soft - hard crude / refined / modified	
Palm oil	Tallow
Soy bean oil	Lard
Rapeseed	Milk fat
Palm kernel oil	Fish oil
...	...
Derivatives: fatty acids and fatty acid esters monoglyceride/ diglyceride mixtures ...	
Application:	
- food industry - salad / dressing oils (oleines) - margarines, shortenings - frying / cooking oils - confectionery (CB replacement fats) - pastry, bakery products	
- cosmetics / pharmaceutical industry	
- oleochemical industry	
- chemical industry	
-....	

There are three stages in the crystallization process which are respectively supercooling of the melt, nucleation and crystal growth. The crystals normally do not remain single but tend to agglomerate.

The key point in fractionation is the selectivity of crystallization which is determined by the way the oil is cooled. It is a general belief that the slower the crystallization, the bigger the crystals and the higher the selectivity. However, more important than the crystal size is the uniformity in size and texture as well as their resistance against mechanical stress.

The selectivity of crystallization is determined by the degree of compatibility of the different triglycerides in the solid state which in turn is a function of the crystal form and of the composition. How far this selectivity is determined by the cooling conditions depends not only on the overall cooling rate but also on the specific technical

features of the crystallizer vessel: the heat transfer characteristics as well as the homogeneity of the crystallizing slurry are key factors in the control of the crystallization process through its successive stages.

Table 3: Physical properties of polymorphic forms

	polymorphic form		
	α	β'	β
melting point	Low-----> High		
melting enthalpy	L -----> H		
stability	L -----> H		
selectivity	L -----> H		
activation energy	L-----> H		
	H <----- L	nucleation rate	
	H <----- L	crystallization rate	
	H <----- L	miscibility in solid state	
	H <----- L	triglyceride compatibility	
	α	β'	β

a. Nucleation

Normally, prior to crystallization, the oil is heated to a temperature above the final melting point of the oil, in order to fully destroy the crystals present in the oil phase. Thereafter, the oil is cooled in a controlled manner according to a given cooling profile: this cooling curve is not only dependent on the raw material and the required end products, but is also largely determined by the technical features of the fractionation equipment.

Nucleation occurs when the melt is far from the thermodynamic equilibrium i.e. when the melt becomes supercooled.

Three types of nucleation phenomena can occur. Homogeneous nucleation takes place in the bulk of the mother phase. Heterogeneous nucleation refers to the formation of nuclei onto foreign substances. Secondary nucleation appears when tiny crystallites are removed from the surface of existing crystals, which in turn act as new nuclei.

In many real systems, heterogeneous nucleation occurs before homogeneous nucleation. It takes place at solid particles for which the new phase has some chemical or physical affinity, such as dust particles, walls of crystallizers or foreign material.

b. Crystal growth

Once the nuclei are formed, they grow further. The rate with which they further develop depends not only on external factors (degree of supercooling, presence of inhibitors...), but also on internal factors (polymorphic form, crystal morphology, crystal defects...).

The growth rate is proportional to supercooling and inversely proportional to viscosity. The higher the viscosity, the more difficult the exchange of material between the bulk phase and the crystal surface and the slower the crystals grow.

Similarly, the transfer of crystallization heat from the crystal surface to the cooling surface is negatively affected by viscosity. In order to allow a continuous and uniform crystallization, the fatty matter needs to be kept homogeneous. This requires an intense but not destructive agitation.

During cooling and subsequent crystallization, the viscosity increases. The viscosity is not only a result of the increasing amount of solids present in the liquid phase but is also influenced by the crystal size distribution as well as the interactions between the different crystals.

c. Agglomeration

Due to attractive interactions between crystals, they tend to form clusters. The very large crystals which can be observed during crystallization are often composed of different small crystals which are held together by weak bonds. Agglomeration, however, can lead to a lower separation efficiency due to a higher entrainment of liquid inside the clusters. Depending on how these crystals are submitted to mechanical stress, they may partially desintegrate which, in turn, can lead to the formation of tiny stearic particles in the olein phase. These very small particles are sometimes difficult to remove from the liquid, causing poor cold stability of the liquid fraction.

d. Morphology

The crystal morphology is determined by internal as well as external conditions. The overall crystallization kinetics depend on the rate of formation of nuclei as well as on the rate at which these centers of crystallization grow. The size and shape of the ultimate crystals depend on the relationship between these two factors.

Normally, slow cooling results in large crystals, whereas fast cooling gives smaller crystals. The crystal size is not so important as is generally stated. The optimal crystal size is largely determined by the separation technique, more specifically the fineness of the filter belt or filter cloth. More important than the size, however, is the uniformity in crystal size and shape as well as the resistance against mechanical stress. To reach this state, a controlled initiation and selective crystallization is required.

2. Separation

The efficiency of fractionation is not only determined by the crystallization behaviour during the cooling sequence, but also by the separation conditions. There are several separation systems in use in the oil fractionation industry (table 4).

Most of the dry fractionation installations operate with a filter. There are two different filtration techniques, vacuum filtration and press filtration. The driving force for filtration is function of the differential pressure applied to the slurry either by means of a partial vacuum at the filtrate side or a pressure at the slurry side.

Table 4: Separation techniques used in fractionation industry

Separation techniques	
Filtration - vacuum:	- rotary drum filter
	- belt filter
	- press : - membrane press filter
	- hydraulic press
Centrifugation	
Decantation	

Vacuum filtration

The two most commonly used vacuum filters are the rotary drum filter and the belt filter (figure 1). Both are continuous filters, in which the liquid phase is separated from the solid part under reduced pressure. In order to allow continuous operation, three stages can be defined in a vacuum filtration. In a first stage, the crystals are concentrated on the filter medium (stearin cake building), by suction of the liquid or olein phase through the solids and the filter medium. The cake is subsequently dried by allowing air (or nitrogen in the case of oxygen sensitive products) to pass through the concentrated crystal mass. Thereafter, the cake is discharged from the filter medium by counterblowing with air and subsequent scraping.

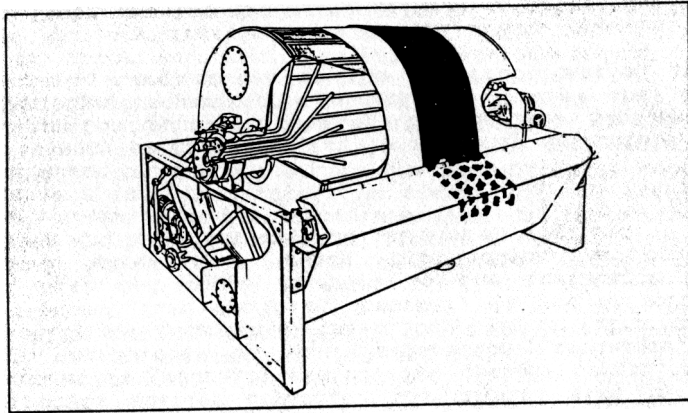
The filtration rate and the yield are very dependent on the crystal morphology and especially on the crystal size. The finer the crystals and the broader the crystal size distribution, the lower the filtration rate. Also the density of the crystals has an impact on the yield: the less dense the intracrystalline matrix is packed together, the more olein remains entrained within the crystals, which in turn negatively affects the yield.

Due to the restricted differential pressure, (maximum 0.5-0.7 bar for most industrial vacuum filters), vacuum filters are commonly equipped with a filter cloth or a filter belt with high permeability and hence large pore size. This in turn requires large crystals, to minimize passage of crystals through the filter medium. This is one of the basic reasons why in the past, the cooling conditions were set towards the formation of large crystals. It is principally the stearin cake which acts as a filter medium instead of the filter cloth.

Press filtration

In order to overcome certain disadvantages of vacuum filtration, more and more dry fractionation processes are equipped with a membrane press filter (figure 2). A membrane press filter consists of a series of filter chamber plates which are kept together by means of a hydraulic cylinder. The available filter surface is much larger than a vacuum filter, allowing a much faster and more uniform filtration (vacuum filter $\approx 6\text{m}^2$ \leftrightarrow membrane press $\approx 60\text{m}^2$).

Rotary drum filter (Amafilter)



Vacuum belt filter (Florentine filter)

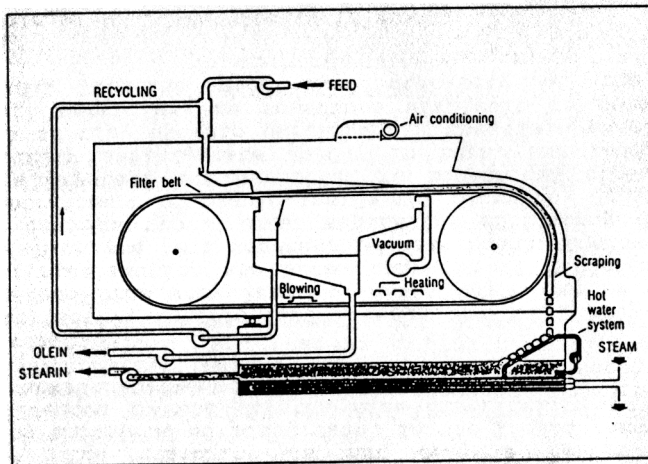
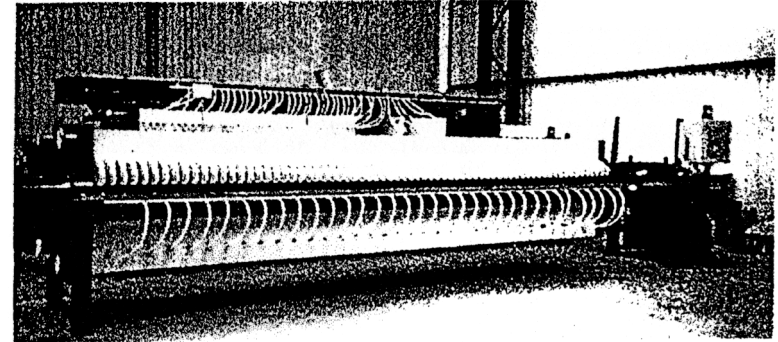


Figure 1: Schematical presentation of the two most common types of vacuum filters used in fractionation

SIDE BAR FILTER



TOP BAR FILTER

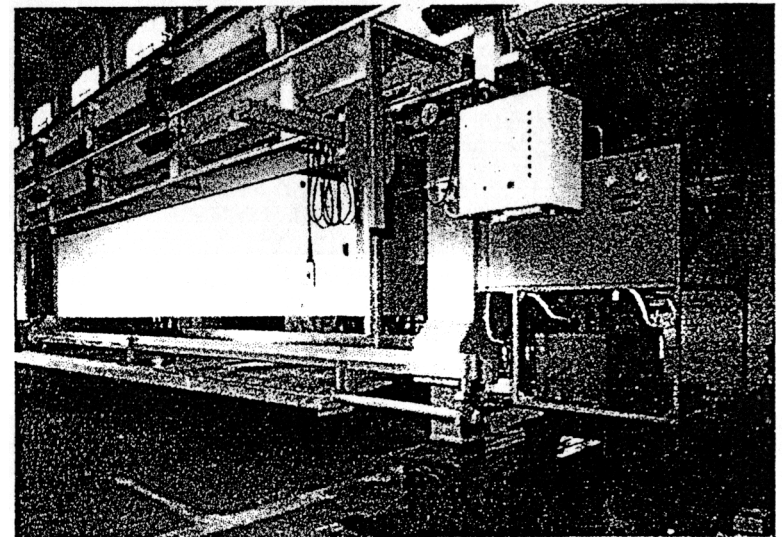


Figure 2: Membrane filter presses with side bar and top bar plate support