step, the crystals are mechanically squeezed in order to extract part of the olein which is entrained in the solid mass. The filtration curves are important in optimizing the crystallization conditions, as they directly reflect the separation efficiency of the olein/stearin mixture.
From a technological point of view, the filtration curves also reveal important information: on the basis of the relative amount of olein, liberated during filling of the filter, the relative size and hence capacity of the filter can be calculated.

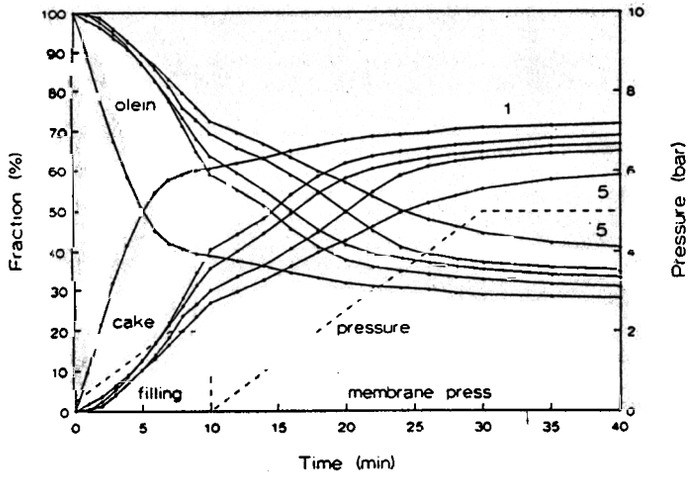



Figure 10: Membrane press filtration curves of milk fat

The efficiency of fractionation is determined by the quality of the final products, obtained after separation. Most of the analytical methods, used to express the quality of a fractionated product, are physical methods. In table 10, some physico-chemical parameters of the milk fat olein and stearin fractions, obtained after press filtration, are represented.
On the basis of these results, the correctness of the cooling profile and hence selectivity of the crystallization process can be deduced.

In figure 11, the SFC-curves of the different oleins and stearins, obtained after press filtration, are given as a function of the temperature. The use of pulsed-NMR to determine the physical behaviour of an oil or fat has become a commonly accepted technique. Although the SFC data reflect the behaviour of the amount of solid as a function of the temperature, they cannot be extrapolated as such to the crystallization characteristics of the given sample. The way the samples are thermally treated largely affects the SFC measurement. It is therefore of great importance to follow accurately the method in order to obtain comparable data.



Table 10: physico-chemical characterization of the olein and stearin fractions obtained after press filtration

| Sampling time | Yield olein % | Olein CP °C | Olein MP °C | Olein DP °C | Olein IV | Stearin CP °C | Stearin MP °C | Stearin DP °C | Stearin IV |
|---|---|---|---|---|---|---|---|---|---|
| Initial milk fat | | 17.5 | 34 | 32.5 | 38.5 | | | | |
| 2hr 21°C | 72 | 11.5 | 23 | 22 | 41.5 | 26 | 43 | 42 | 31 |
| 2hr 17°C | 67 | 10.5 | 18.5 | 17.5 | 42.5 | 25.5 | 42 | 41 | 31.5 |
| 2hr 15°C | 59 | 10 | 17 | 16.5 | 43 | 24 | 41 | 40 | 32.5 |

CP: cloud point; MP: melting point;
DP: dropping point; IV: iodine value

The pulsed NMR also allows a quick but quite accurate estimation of the yield. By measuring the SFC of the slurry, prior to filtration, and of the stearin cake, at the end of filtration, the yield can easily be calculated (table 11):

$$\text{Yield stearin}(\%) = \frac{\text{SFC slurry}}{\text{SFC cake}} \times 100$$

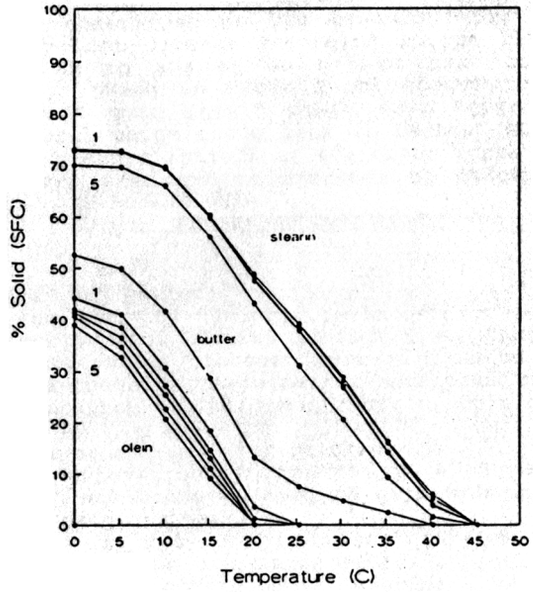
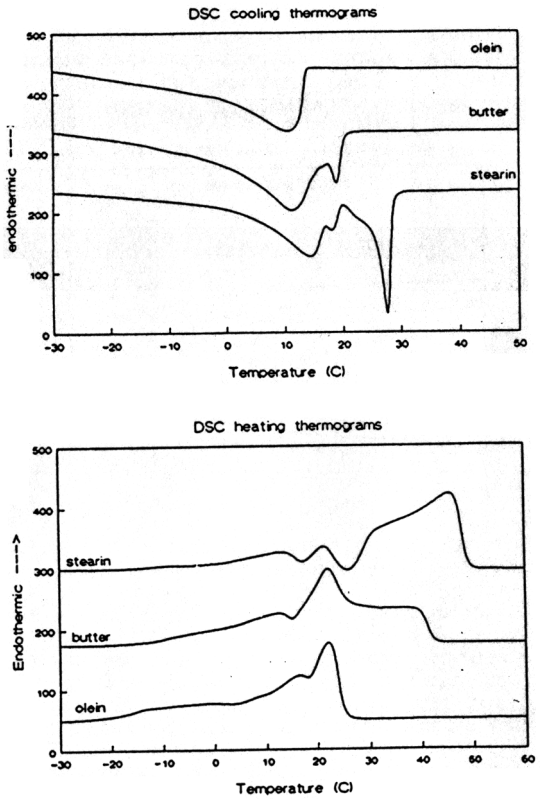



Figure 11: Solid fat profiles of the different milk fat fractions obtained by dry fractionation

Table 11: SFC data and yields of different membrane press filtrations

| Sampling time | Yield olein % | SFC slurry % | SFC cake % | Calculated Yield % |
|---|---|---|---|---|
| 2hrs 21°C | 72 | 12.5 | 43 | 71 |
| 2hrs 17°C | 67 | 15.5 | 45 | 65.5 |
| 2hrs 15°C | 59 | 16.5 | 40 | 59 |

Figure 12 represents some differential scanning calorimetric thermograms of the different phases. In contrast to most analytical methods which only reflect a single value, DSC reveals much more information with respect to the overall melting and crystallization behaviour.




igure 12: DSC melting and cooling thermograms of milk fat and its olein and stearin fractions



During fractionation, the chemical composition of the liquid and solid phase continuously changes. As crystallization proceeds, the more saturated triglycerides are gradually concentrated in the solid phase, leaving behind a more unsaturated liquid phase.
HPLC and GLC are normally used to determine the glyceride and fatty acid composition. In figure 13, a typical HPLC and GLC chromatogram of the milk fat is given.

The implementation and systematic use of physical and chemical analytical methods allows a better understanding of the nature of the fractionation process. This in turn makes optimization of the fractionation process towards final product quality and yield in end products, as well as production efficiency of the plant faster and easier.

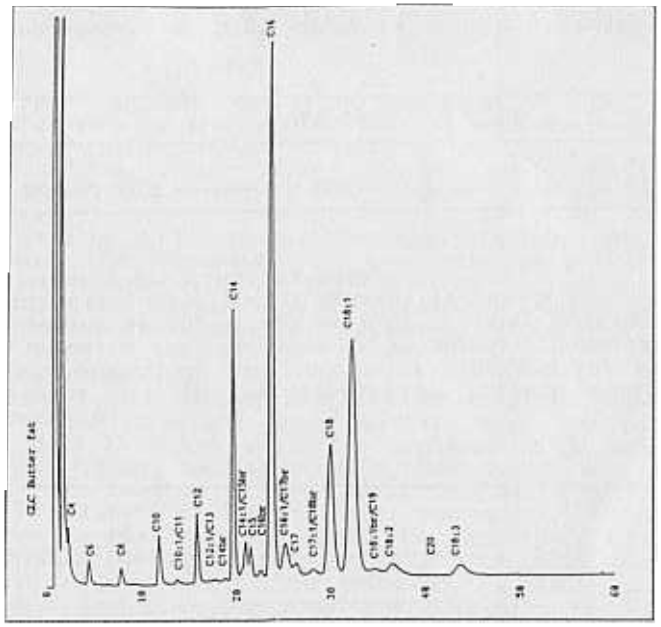
## Fractionated products

Oils and fats are complex mixtures of glycerides which are composed of a whole variety of different fatty acids. The most important fatty acids found back in nature, are palmitic acid (C16), stearic acid (C18), oleic acid (C18:1) and linoleic acid (C18:2). Based on these fatty acids, the triglycerides which make up to 95% of an oil or fat, can be generally divided into four classes according to the type of saturated fatty acids esterified on the glycerol unit. These are the trisaturated (SSS), disaturated/mono-unsaturated (SSU-SUS), monosaturated/diunsaturated (SUU-USU) and the fully unsaturated triglycerides (UUU).
These triglycerides exhibit a different physical state and hence potential for end-use application (table 12).

Table 12: Properties of different triglyceride types

| Triglyceride type | physical state | application |
|---|---|---|
| ->SSS | solid | fatty acid production hard coatings... |
| ->SSU-SUS<- | solid->semisolid | confectionery... |
| ->SUU-USU<- | semisolid->liquid | margarines... |
| ->UUU | liquid | salad (dressing) oils liquid frying oils... |

This simplified scheme is not applicable to fats and oils which are rich in short and medium chain fatty acids. Palm kernel oil and coconut oil, for example, which are rich in lauric acid (C12) and myristic acid (C14), will have properties similar to the SSU/SUS group, whereas the oils rich in C8 and C10 fatty acids, have many properties similar to the SUU/USU group.



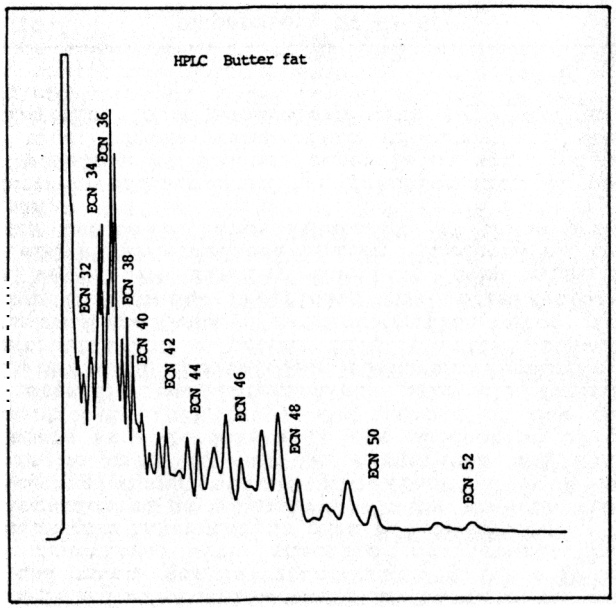



Figure 13: GLC chromatogram of the fatty acid composition and HPLC chromatogram of the triglyceride composition of milk fat



## 1. Vegetable oils

*Palm oil*

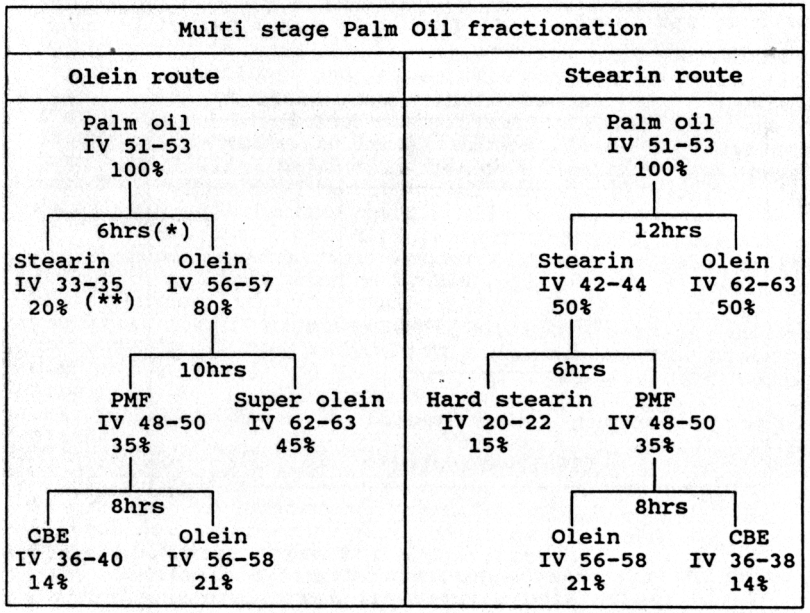
Palm oil is by far the most important fractionated oil. There are industrial fractionation installations in operation which process up to 2000 tons of palm oil per day. Both crude as well as refined palm oil are fractionated, the latter being the most frequent case.

The main objective is to obtain olein fractions with a low cloud point and good cold stability. Single stage fractionation yields oleins with a cloud point below 10°C and a stearin with melting point 44-52°C. The oleins are used as a substitute for soft oils in cooking and salad oils, whereas the stearin fractions find applications in frying fats, margarines and shortenings.

**Single stage palm oil fractionation**

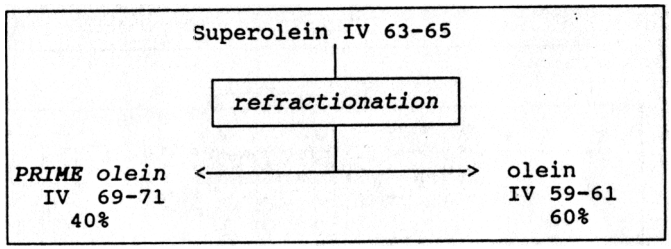
| Palm oil | Olein IV | Olein CP | Stearin IV | Stearin MP | Yield % olein | cycle time (*) |
|---|---|---|---|---|---|---|
| IV 51-53 | 56-57 | 7-9 | 33-35 | 52 | 75-80% | 6 hrs |
| CP 21°C | 59-60 | 4-5 | 38-40 | 50 | 60-65% | 8 hrs |
| MP 42°C | 62-63 | < 3 | 42-44 | 46 | 45-50% | 12 hrs |

**Multi stage Palm Oil fractionation**




(*): cycle times in a De Smet fractionation
(**): results from 6 bar membrane press filtration

Together with a further development of the single stage palm oil fractionation process, there is an increasing tendency to double and even triple fractionate palm oil in order to produce fractions with specific characteristics: high IV superoleins and intermediate palm oil fractions.
Refractionation of the low IV olein or stearin from the first separation, produces a palm mid fraction or a soft stearin which can be used as such in margarines and shortenings or which serves as a feedstock in the production of cocoa butter replacement fats (CBE fats). An example of how the different oleins, stearins and intermediate palm oil fractions can be obtained, is given above (olein route and stearin route).
The construction of a proper fractionation pathway is not an easy task since every refractionation step involves the production of two new fractions. The optimization is in most cases a matter of finding the best compromise between the quality of the intermediate and end products on the one hand, and of the useability and saleability of those products on the other hand.
The latest developments in the fractionation of palm oil have made it possible to produce superoleins with iodine values of 70 and more. These prime olein products are obtained by a refractionation of a superolein with IV > 63. An example is given below.



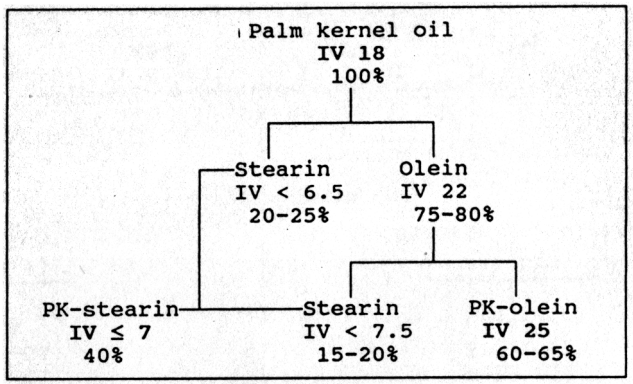

***Palm kernel oil***
Palm kernel oil is fractionated to produce stearins which after hydrogenation, are used as a high quality hard butter oil or covering fat. The stearin is normally produced in a dry process using labour intensive high pressure hydraulic presses or in miscella using costly solvent fractionation. Palm kernel oil is usually fractionated crude.

| Palm kernel oil ——————> Olein | | Stearin | Yield % stearin |
|---|---|---|---|
| IV 17-19 | IV 24-27 | IV ≤ 7 | ≥ 40% |

The development of high pressure membrane presses together with a better insight in the specific crystallization behaviour of palm kernel oil, has overcome certain



disadvantages inherent to above mentioned techniques. Today, it is possible to dry fractionate palm kernel oil in a similar way as palm oil, in modified crystallizers using 25 bar membrane press filters.




***Soybean oil***
With an iodine value of around 135, soybean oil is a soft oil, which is very rich in polyunsaturated fatty acids (about 45-55% Linoleic acid and 5-10% linolenic acid). This makes the oil quite sensitive to oxidation. In order to improve its shelf life, the oil is partially hydrogenated. Hydrogenation, however, causes formation of higher melting triglyceride substances, which makes the oil unsuitable for certain markets. It is therefore fractionated in order to remove the solids from the partially hydrogenated oil.

To produce salad oils with a good cold stability, the oil is usually hydrogenated to an IV of 100 to 115 (reduction of linolenic acid content to 2-3%), after which the oil is winterised at very low temperature (2-5°C). For cooking and frying oils, soybean oil is more intensively hydrogenated below an IV of 90 in order to improve its oxidative stability (linolenic acid content < 0.5%). The stearic fractions obtained from fractionation of such hydrogenated oils, are a good base for shortenings or margarines or find application as cocoa butter replacement fats.

## 2. Animal fats

***Milk fat***
Milk fat is characterized by an enormous variability in composition and hence physical behaviour, due to seasonal influences, feed patterns of the animals as well as origin of the bovines.

| Soybean oil IV 135 | Olein Yield % | IV | CP °C | CT* hrs | Stearin IV | DP °C |
|---|---|---|---|---|---|---|
| hydrogenation | | | | | | |
| —IV 115 | 85-90% | 119 | -11 | > 24 | 98 | 33.5 |
| —IV 109 | 75-80% | 114 | -10 | 18-24 | 92 | 34.5 |
| —IV 97 | 65-70% | 104 | -9 | 12-18 | 84 | 35.5 |
| —IV 85 | 50-55% | 94 | -7 | < 5 | 75 | 36.5 |
| —IV 75 | 40-45% | 84 | -5 | < 2 | 68 | 37.0 |

IV: iodine value; CP: cloud point; DP: dropping point; CT: cold test

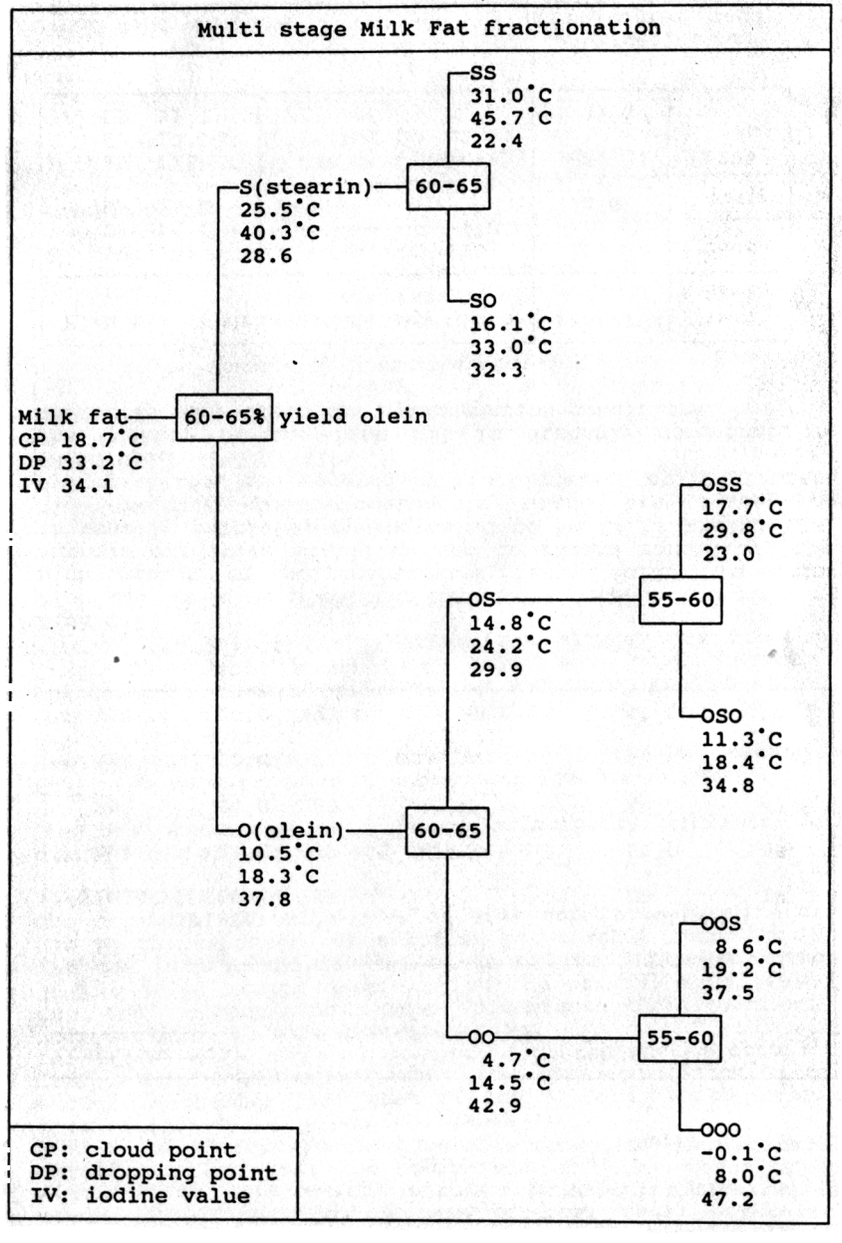
(*) The olein quality is usually determined by means of a cold test at 0°C. The cold test, however, is not only determined by the iodine value of the olein fraction, but it is strongly related to the performance of the hydrogenation process. Especially formation of trans isomers, which frequently occurs during hydrogenation, largely affects the olein quality with respect to its cold stability.

In order to obtain a product of constant quality with physical characteristics that remain unchanged all year round, milk fat is being fractionated and reblended according to the required physical specifications.
Beside the consistency aspect, special milk fat fractions find an increasing application in a whole variety of food products:
- puff pastry requiring high melting point stearins
- low fat butter with 40% milk fat in which stearins are used
- soft butters with improved spreadability requiring low melting point fractions
- special butter fractions for confectionery
- ice cream containing olein fractions
- Danish cookies with milk fat mid fractions
- reduction of blooming properties of chocolate using stearins and intermediate fractions
- liquid cooking butter oil

The high price of milk fat definitely justifies the very strict quality standards imposed by industrial users. A very wide range of products can be obtained by simple or multiple fractionation. An example of a multi stage fractionation of a milk fat is given below.

Milk fat can be fractionated from various products:
- anhydrous milk fat from butter
- anhydrous milk fat from cream
- unwashed milk fat
- deodorised milk fat





*Tallow*
Besides milk fat, there are two other important animal fats which are processed in the food industry: beef tallow and lard. Although these animal fats have lost a lot of their importance due to competition with palm oil, they are still widely used in frying and bakery products.
Tallow has a quite high melting point which can vary between 42 and 48°C, depending on the season, feeding pattern and animal's quarter. The main interest of tallow fractionation is the production of similar fractions throughout the year as well as of lower melting olein fractions. Depending on the olein's melting point, fractionation is conducted in one or two steps. An example of both is given below.

**Fractionation** — Tallow (DP 43°C, IV 47)

| Yield ± | Olein DP | Olein IV | Stearin DP | Stearin IV |
|---|---|---|---|---|
| 85% | 38°C | 50 | 53°C | 30 |
| 70% | 33°C | 53 | 51°C | 34.5 |
| 60% | 28°C | 54.5 | 50°C | 36 |
| 45% | 22°C | 56.5 | 48°C | 38.5 |

**Refractionation** — Tallow olein (DP 31°C, IV 54)

| Yield ± | Olein DP | Olein IV | Soft Stearin DP | Soft Stearin IV |
|---|---|---|---|---|
| 80% | 22°C | 56.5 | 41°C | 42 |
| 75% | 20°C | 57.5 | 40°C | 43 |
| 70% | 17°C | 58 | 39°C | 45 |
| 65% | 15°C | 58.5 | 37°C | 46 |
| 50% | 14°C | 59 | 34°C | 49 |

*Lard*
In contrast to tallow, which is quite easy to fractionate, lard is much more difficult to fractionate due to its sharp melting and crystallization profile. However, it can be fractionated more easily after interesterification or after partial hydrogenation. Depending on the required olein quality, fractionation is done in a single or double stage.

**Fractionation** — Lard (interesterified) (DP 33°C, IV 62)

| Yield ± | Olein DP | Olein IV | Stearin DP | Stearin IV |
|---|---|---|---|---|
| 80% | 27°C | 67 | 50°C | 45 |
| 70% | 24°C | 69 | 48°C | 47.5 |
| 65% | 20°C | 71 | 47°C | 48.5 |
| 50% | 16°C | 73.5 | 45°C | 50 |

*Fish oil*
Fish oil is a very particular product as it contains a very high amount of polyunsaturated fatty acids. In order to improve oxidative stability and to retard rancidity, the oil is usually partially hydrogenated to an IV of around 120. The high melting point components which are formed during hydrogenation, are removed by fractionation at low temperature (5-15°C).
The quality of the fish oil is strongly dependent on its origin as well as on the hydrogenation conditions.

| Fish oil (hydrogenated) --> | | Olein | Stearin | Yield % olein |
|---|---|---|---|---|
| a | IV 124 | 135 | 105 | ±60% |
| | CP 14°C | -4°C | | |
| | DP 28°C | | 34°C | |
| b | IV 115 | 129 | 84 | ±70% |
| | CP 17°C | -2°C | | |
| | DP 31°C | | 37°C | |

3.Non food products
Apart from the products discussed above, there is a whole variety of other fatty matters, used in both the food and non food industry, which are fractionated using the dry fractionation technique. An example of some of these less common fatty matters are given below.

*Fatty acids and derivatives*
Fatty acids are normally separated by distillation under reduced pressure, according to their carbon number into short chain (C12), medium chain (C14) and long chain components (C16, C18). Separation of saturated from the unsaturated fatty acids, however, as for example stearic acid (C18) and oleic acid (C18:1), cannot be achieved in by distillation due to the very small differences in boiling point.
Today, most of the fractionation systems used to separate these fatty acids, employ either a solvent or a detergent. These substances, however, can also be fractionated in a much cheaper way using the dry fractionation technology. Some typical examples are given below.

| Initial product | Olein | Stearin | Yield % olein |
|---|---|---|---|
| Tallow fatty acids<br>IV 45<br>CP 38°C<br>DP 47°C | IV 83<br>CP 5°C | IV 17<br><br>DP 58°C | 40-45% |
| Fatty acid esters<br>IV 41<br>CP 11°C | IV 60<br>CP -1°C | IV 8<br>CP 24°C | 60-65% |

*Mono/di/triglycerides mixtures*
Other products of interest are the partially hydrolysed oils, which are used in the cosmetic and pharmaceutical industry. During partial hydrolysis of soft oils as for example corn oil and soy bean oil, the triglycerides are transferred into a complex mixture of mono-, di- and triglycerides. During this hydrolysis, high melting point glycerides are formed which need to be removed in order to obtain a fully liquid oil with good cold stability.

| MG/DG/TG mixture 36-48-16 % (W/W) | Olein | Stearin | Yield % olein |
|---|---|---|---|
| IV 114<br>CP 16°C<br>DP 23°C<br>MP 38°C | IV 120<br>CP -8.5°C<br>DP 3.5°C<br>MP 7°C | IV 97<br>CP 30°C<br>DP 44°C<br>MP 48°C | 70-75% |



## Conclusion

The separation of fatty matters using dry fractional crystallization has gained an important position in the oils and fats industry. Its major advantage is the purity and reversibility of the process beside the very low processing cost. The continuous development on both products as well as the technological level reached, have made it an attractive alternative to other more costly processes.

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