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ALTERNATIVES TO HYDROGENATION

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Why alternatives?

Partial hydrogenation leads to the formation of *trans*-isomers and if a consumer wants to avoid these, he has to look for alternatives. He could eat less fat, avoid dairy products and meat from ruminants and switch to liquid margarine or oil when this is technically possible. However, by product development the edible oil industry can also provide the consumer with products with reduced *trans*-isomer content. I will now discuss two tools available for this development: interesterification and fractionation, and I will also provide some examples.

Interesterification

Three different interesterification processes are used industrially:

- randomization by chemical catalysis;
- directed interesterification using a catalyst that is active at low temperature;
- enzymatically catalysed interesterification.

The first two processes invariably use triglycerides as starting material and merely redistribute the fatty acid moieties over these triglycerides. Accordingly, the fatty acid composition does not change on interesterification but carbon number and partition number distributions do. Physical properties like melting point, solid fat content (SFC) and the tendency to recrystallise also change which is why the process is used in the first place. Lipase catalysed interesterification processes on the other hand, also aim at changing the fatty acid composition of the triglyceride substrate.

Randomization by chemical catalysis

Industrial randomization processes use a strongly basic catalyst such as sodium methylate. Since this catalyst will be inactivated by water and fatty acids, some caustic soda is added to the starting material to alkalinity. Then it is rigorously dried under vacuum, usually at 80-100°C and only then is the catalyst added; a reaction time of 15-30 minutes suffices to approach equilibrium.
The catalyst is inactivated by the addition of water which, if acidified, causes the free fatty acids and fatty acid methyl esters to concentrate in the oil phase; the subsequent deodorisation process will see to their removal. Since one mole of catalyst (MW 54) leads to the loss of two moles of

fatty acids (MW 284), proper oil pretreatment not only saves on catalyst usage but also on product yield; 0.10 wt% catalyst should suffice.

US literature mentions the retardation of lard recrystallisation as example of randomization. In Europe, the process is used for preparing a hardstock for health and reform margarine fat blends by interesterifying a fully hydrogenated lauric oil (melting point about 35°C) with a fully hydrogenated vegetable oil (melting point above 60°C) or palm stearin. Partially hydrogenated sunflower seed oil is also interesterified with liquid oil and/or palm oil to increase chain heterogeneity and thereby reduce the rate of recrystallisation and its formation of “sandiness”.

Directed interesterification

In this process the highest melting triglycerides are being withdrawn from a randomizing melt by crystallisation. This withdrawal upsets the equilibrium distribution as a result of which more of these high melting triglycerides are being formed. The crystallisation requires a lowish temperature at which the catalyst must still be active; alkali metals meet this requirement. Catalyst inactivation must be carried out at low temperature but thereafter the fat can be heated and fully melted to allow water-washing.

In the US, directed interesterification is mentioned again for lard and in Europe, the only application I am aware of is the directed interesterification of sunflower seed oil to produce a health margarine fat blend that is *trans*-isomer free and very low in saturated fatty acids. Extremely careful pretreatment of the oil, safety measures for handling alkali metals and the long (6-72 hours) reaction time make the process quite a bit more expensive than the randomization process.

Enzymatically catalysed interesterification

This process relies upon the 1,3-specificity of the lipase enzyme to substitute fatty acids in the -position of triglycerides. It is used in Japan and the Netherlands to manufacture cocoa butter equivalents (symmetrical mono-unsaturated triglycerides) from either palm mid fraction or high oleic sunflower seed oil by the introduction of stearic acid. In practice, some hydrolysis cannot be avoided. This leads to some loss of specificity by the isomerisation of partial glycerides and also necessitates the removal of these partial glycerides from the reaction product. This removal can be by enzymatic hydrolysis using a lipase with strong preference for partial glycerides; solvent fractionation using a somewhat polar solvent is another way.

In the course of the enzymatically catalysed interesterification, an equilibrium is approached whereby the composition of the 1,3-bound fatty acids equals that of the free acid moieties. Consequently, the triglyceride reaction product still needs purification by fractionation. In addition, the free acid moieties need purification or hydrogenation before they can be recycled to the interesterification stage. All this makes the process quite expensive so that it is only used for high-value products such as cocoa butter equivalents and special components of infant formulae.

Fractionation

Fractionation processes for edible fats aim at separating a starting material into a low melting fraction (olein) and a high melting fraction (stearin). All industrially used processes have in

common that the temperature of separation determines the olein properties and that the olein content of the filter cake is the main factor determining the stearin properties and the yields of both fractions. The performance of a fractionation process is commonly described by quoting iodine values (IV) since these are linearly additive.

When assessing fractionation processes, attention should not only be paid to properties and yield of the fraction of main concern but also to the other fraction or fractions (the by-products), their value and the possibility to recycle them. This is especially important when fractionating high cost raw materials, where the fraction of main concern has to bear the depreciation cost of the by-products.

Solvent fractionation

In this process, the starting material is dissolved in a solvent like acetone or hexane and then the solution is cooled so that triglycerides with the highest melting point start to crystallise. Crystals formed are separated by filtration and the fractions are recovered by solvent evaporation. Because the liquid present in the filter cake is a diluted olein solution, even a wet cake contains little olein so that the solvent fractionation process is quite “selective”. Besides, washing the filter cake with additional solvent can reduce its olein content even further. Another advantage of the solvent fractionation process over the dry fractionation process operating from the melt, is the high degree of crystallisation attainable: a high IV olein can be produced by solvent fractionation in a single operation but requires a multi-step operation in the dry fractionation process.

On the other hand, the investment in a solvent fractionation plant is high. It has to handle large volumes of diluted solutions and has to be explosion proof. Operating costs are also high because cooling to low temperatures and solvent evaporation are energy intensive. Accordingly, solvent fractionation is in practice only used for high added value products such as for instance, cocoa butter equivalents

Dry fractionation

In the dry fractionation process, the starting material is fully melted and then cooled down as a result of which higher melting triglycerides start to crystallise which are then separated by filtration. Since the olein in the filter cake is not diluted as in the solvent fractionation process, the dry fractionation process tends to be less “selective”. Several approaches to improve its “selectivity”, or olein content of the filter cake, have therefore been developed.

The oldest approach emphasizes the growth of crystals that lead to a well-draining filter cake and has been supplemented by a filtration system applying suction. A second approach that is hardly used industrially any more, involves mixing an aqueous detergent solution into the partially crystallised melt and concentrating the “washed” crystals into this solution which is then separated centrifugally from the olein.
The most recent approach has shifted attention to the separation stage by the introduction of membrane filter presses to squeeze out as much olein as possible.

However, combining proper crystal development with a highly efficient separation process provides the best of both worlds. By using a screen bowl centrifuge as separator, SFC-values in excess of 70% have been observed for the resulting stearin. Expressed differently, this means about 0.4 part

olein per part of crystalline material whereas a band filter with suction leads to 2.5-3.5 parts of olein per part of crystalline material. It is therefore not surprising that this combined approach has led to the successful development of manufacturing processes for confectionary fats, including cocoa butter equivalents.

Discussion

Having described industrially used interesterification and fractionation processes, I now want to discuss to what extent these processes provide alternatives for the hydrogenation process. In my opinion, they are supplementary tools rather than alternatives. After all, the randomized hardstock mentioned as an example is fully hydrogenated.

In addition, it should not be forgotten that interesterified and fractionated products obtain their consistency from saturated fatty acids. Considering these products as alternatives for partially hydrogenated fats containing *trans*-isomers could, nutritionally, therefore amount to a choice between the devil and the deep blue sea.