

INTERESTERIFICATION AND TAILOR-MADE FATS

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INTRODUCTION

As is widely known, the general term interesterification comprises the formation of new esters existing ones by adding alcohol (alcoholysis), acids (acidolysis) or merely catalyst (interesterification) to a mixture of esters, thereby causing an interchange of acid radicles among the alcohol groups: Fig. 1 shows the process as applied to triglycerides.

A distinction must be made here between intra-molecular interesterification, the interchanging of fatty acid radicles within a triglyceride molecule, and inter-molecular interesterification, in which an interchange of fatty acid radicles takes place between individual triglycerides.

In what follows we shall devote our attention to the latter.

HISTORICAL BACKGROUND

The beginnings of interesterification go back to Duffy, who in 1852 was the first to observe the alcoholysis of triglycerides. However, it was not until Norman's research into interesterification around 1920, which he undertook in connection with the production of butter-like fats, that the process took the decisive turn towards industrial use.

Even so, suitable catalysts had yet to be found to enable this reaction to take place at temperatures at which the undesirable secondary reactions which take place at high temperatures were sufficiently suppressed for the product of the reaction to be regarded as physiologically safe.

Only with the discovery of such catalysts, the glycerylates, by van Loon in 1924, were all the necessary conditions fulfilled for the process to be applied on an industrial scale. Operations in Germany began in

Interesterification

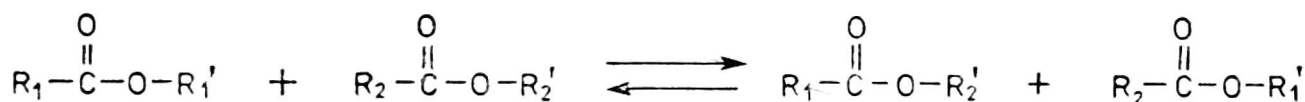
1. Acidolysis reaction



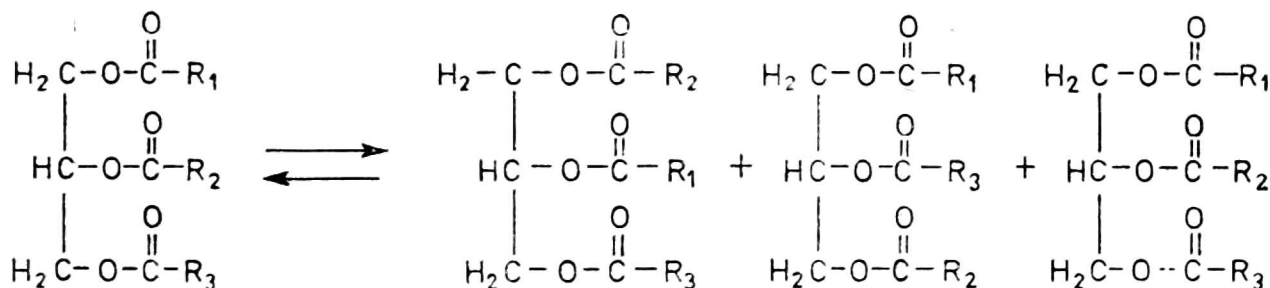
2. Alcoholysis reaction



3. Ester interchange



Intramolecular rearrangement



Intermolecular rearrangement

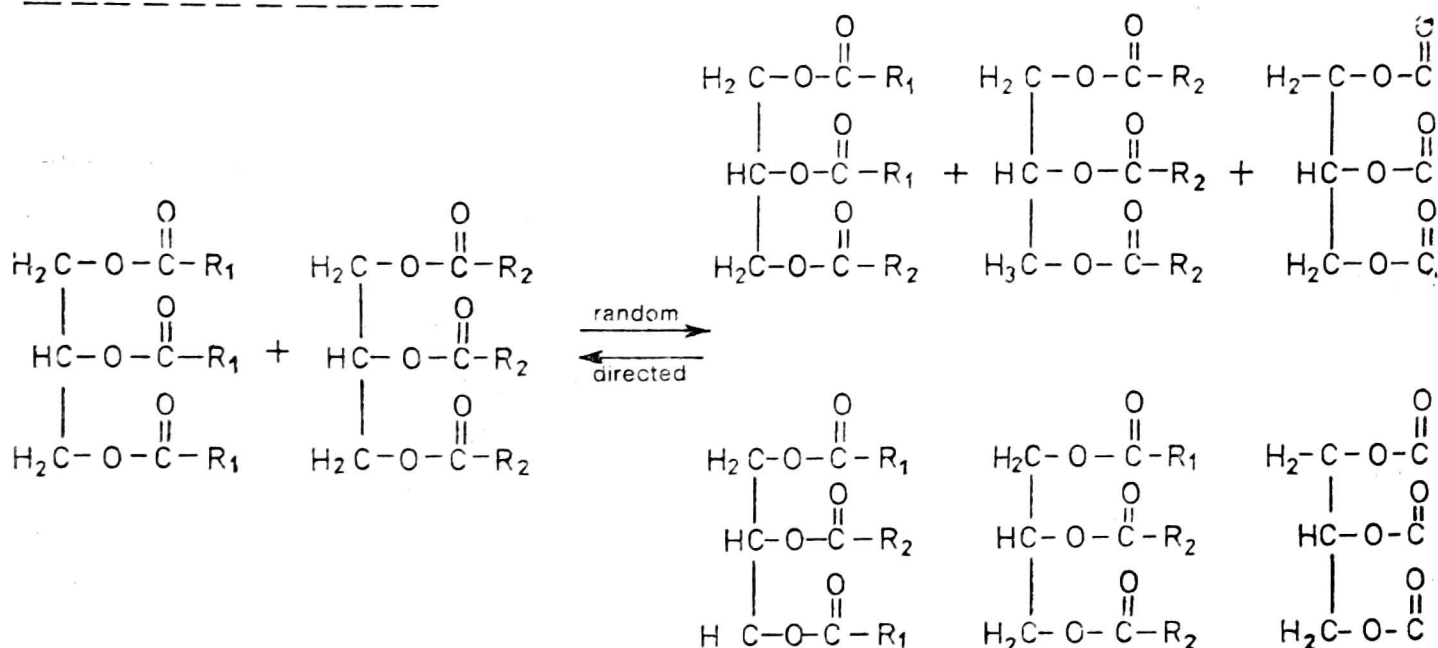


Fig. 1. Reaction in interesterification. After [2]

1931, the aim being to increase the amount of palm oil used in margarine. During the period which followed and throughout the Second World War, intensive research went on in laboratories in many European countries and in America into the subject of interesterification. The results, however, were of little technological significance.

In 1945 Eckey in the USA opened up new areas of application by developing the process of "directed interesterification", especially for lard and the use of new catalysts, in particular the alkali metals. In directed interesterification the reaction takes place below the melting point of one or more of the components involved in the reaction. The latter are removed from the system, allowing the reaction to proceed until the fatty acids concerned are all used up. In this way it is possible to separate mixed triglycerides into high and low-melting fractions.

In the "fifties" other countries started introducing the interesterification process into their production operations, making increasing use of sodium methylate as catalyst instead of the hitherto more usual potassium glycerylate. In Australia, for example, interesterification blends were used on a production scale as cocoa butter substitute and as shortening. Towards the end of the decade Great Britain also started production of cocoa butter substitute and Canada production of interesterified lard. A US patent described the interesterification of mixtures of fats containing palm-oil, in particular for margarine.

At the same time superior-quality margarine was already manufactured with a high proportion of an interesterified blend of palm oil and coconut fat. 1968 saw a technological step forward with the start operations, in Hamburg at the first continuous interesterification plant, using metallic sodium as the catalyst.

Nowadays interesterification plays an economically important part in the industrial preparation of edible fats. Although no precise statistics are available it is safe to say that the total annual production of interesterified edible fats is currently in the region of at least 1 million tons. Of this figure some 200 to 250 thousand tons are produced.

THEORY

As already mentioned, in interesterification *sensu stricto* (i. e. the inter-molecular variety) and exchange of fatty acid radicles takes place between different triglycerides. There are theoretically three possible ways in which the fatty acid radicles can be distributed among the triglycerides. In the case of uniform distribution the available fatty acids are distributed as far as possible among all the triglycerides. With minimum distribution, on the other hand, there should be as many sin-

glycerol-triglycerides present as possible. This is the state of affairs which directed interesterification, of which we have already spoken, is designed to bring about and which occurs as rarely in nature as does uniform distribution. The third case, that of statistical or random distribution as predicted by probability, is shown in Fig. 2, and is the situation aimed for in undirected interesterification.

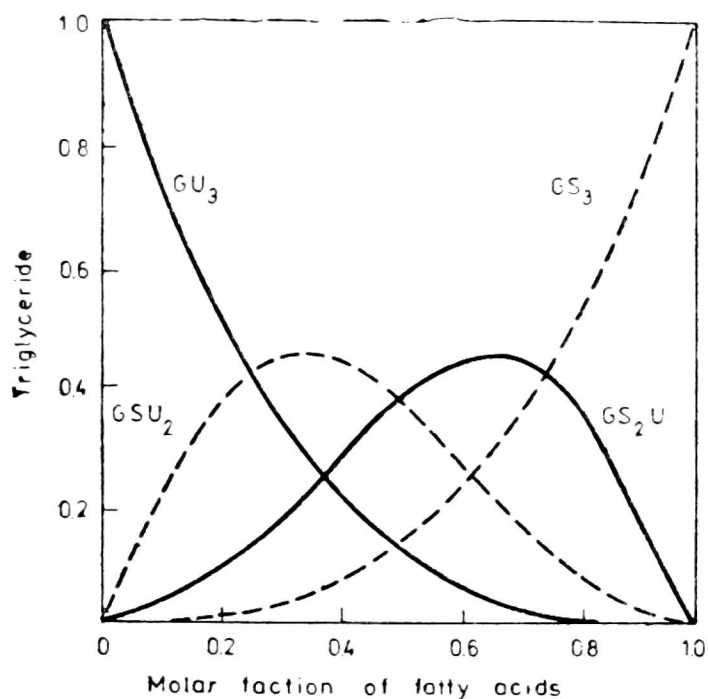


Fig. 2. Random distribution. After [8]

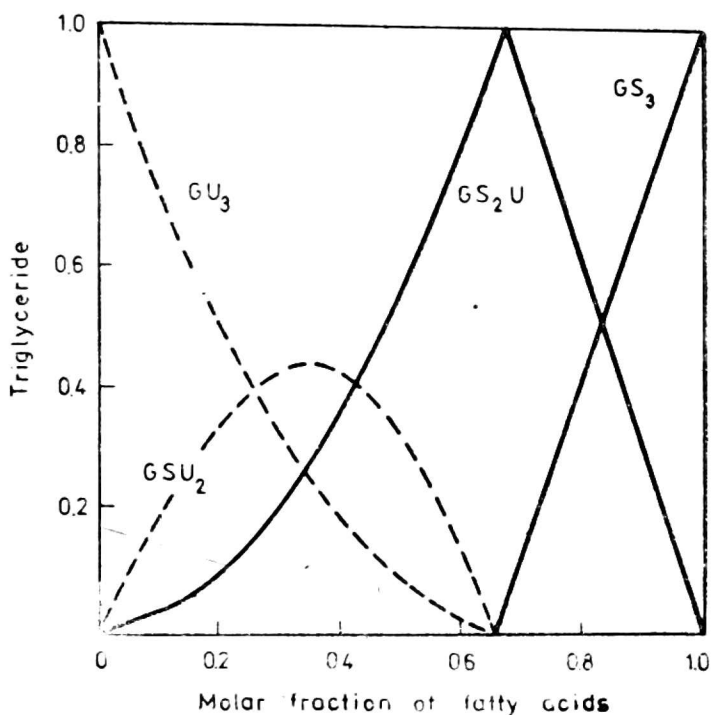


Fig. 3. Restricted random distribution. After [8]

By contrast, it is impossible to arrive at a corresponding classification of fatty acid distribution as it occurs in natural vegetable or animal fats. Although various theories have been put forward, among them that of restricted statistical distribution which is illustrated in Fig. 3, none of them is a true reflection of the situation as it really is. The only thing that can be said with certainty is that the distribution in natural fats appears to range between uniform distribution and restricted statistical distribution, there being evidently no uniform pattern in nature.

MECHANISM

Interesterification, as an entropy-governed reaction, proceeds spontaneously at high temperatures, and it was necessary, as we have seen, to find suitable catalysts before the reaction could be brought about at low temperatures. In addition to alcoholates a whole range of metals such as K, Na, Li, Mg, Zn and Sn were found to be suitable for this

purpose. The current view of the sequence of events in the catalysed reaction is as follows (taking the case of sodium methyrate as an example):

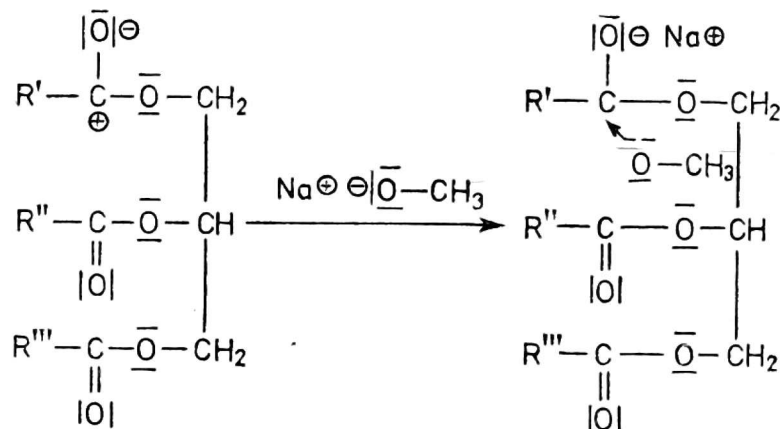


Fig. 4. Catalytic reaction with Na-Methyrate. After [2]

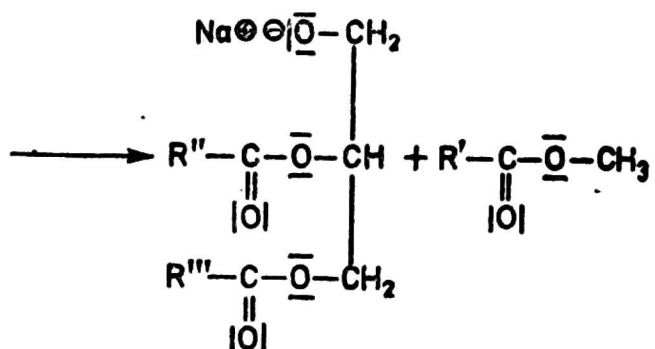


Fig. 5. Active interesterification catalyst. After [2]

The catalyst is first added to the ester group, as in Fig. 4, whereupon the alkoxide group of the ester changes place via this addition compound, as in Fig. 5 with the anion of the catalyst. The newly formed anion can then enter into a reaction with the ester groups of the same or a different glyceride molecule, with an interchange of the acyl groups taking place here again. It should be noted that on the individual glyceride molecule the reaction takes place instantaneously, whereas when interesterifying glycerides mixtures it is necessary to wait some moments in order to give every molecule, on statistical average, the chance of interacting with the catalyst. If interesterification is carried out at the usual temperature of around 100°C secondary reactions such as isomerisation of unsaturated fatty acids and addition and cleavage reaction are of practically no consequence. Thus interesterification is regarded as safe from a nutritional point of view.

INDUSTRIAL PRACTICE AND TECHNOLOGY

The catalyst used in interesterification are by their nature more or less sensitive to acid and/or water. Since the catalysts used nowadays are mainly alkali metals and the alcoholates thereof, the oils of fats involved must first have been alcoholates thereof, the oils of fats involved must first have been subjected to a thorough refining process. The fat should be free from peroxides. Free fatty acids and water should not exceed the standard values of 0.1 and 0.01 per cent respectively. Given these conditions one needs 0.15% of sodium ethylate to produce a good reaction speed, whilst by using metallic sodium as catalyst one can manage on 0.04%, as shown in Fig. 6.

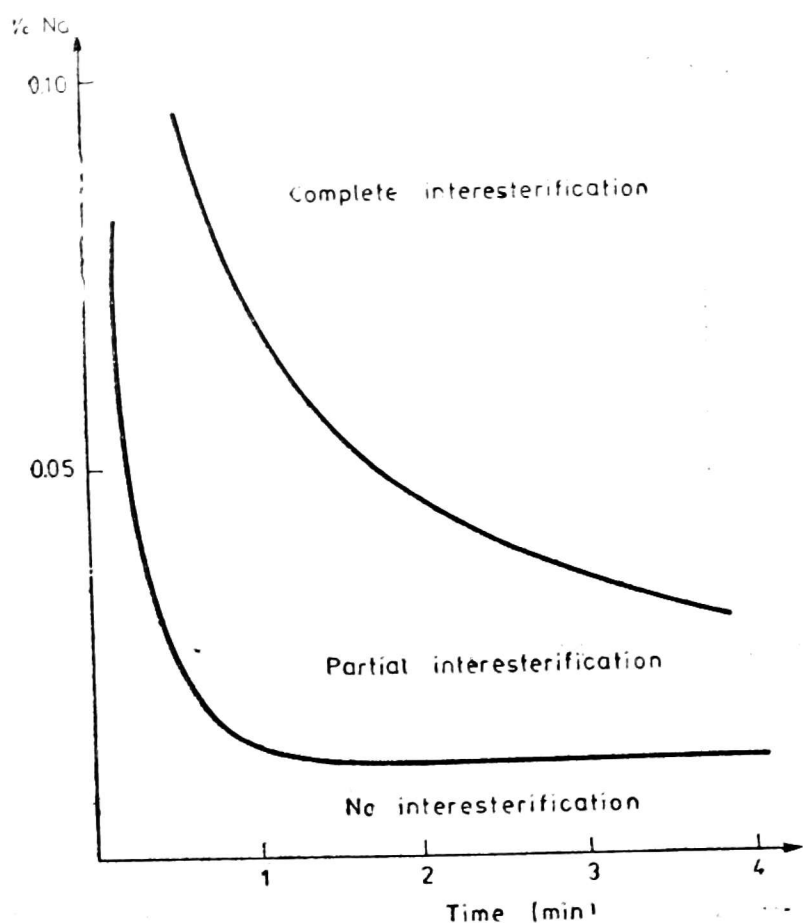


Fig. 6. Influence of catalyst concentration on interesterification speed. After [3]

Apart from its lower cost the use of sodium as catalyst instead of alcoholates has the advantage that it does not involve any losses in the form of methyl or ethyl esters. For health reasons it is essential for any methyl esters to be eliminated completely in the subsequent deodorisation process.

The formation of increased quantities of these esters is also the reason why it is not advisable to add the alcoholates in alcoholic solution, despite the fact that this is easier to manage. There has therefore been a general switch to using these substances in powder form and employing a powerful stirrer to ensure that the catalyst is finely distri-

buted. The metallic sodium which is used as catalyst primarily in continuous interesterification plant is fed as such under pressure into the stream of heated oil (tem. $> 98^{\circ}\text{C}$), where it is likewise finely distributed by means of a homogeniser in order to speed up the formation of the catalytically effective intermediate stage. In this way the reaction with this catalyst reaches equilibrium after only a few minutes.

Batch interesterification can be performed in, for example, the usual closed evacuable stirrer tanks of the type used for neutralisation and bleaching, the powdered catalyst being sucked into the previously dried oil. When the results of interesterification have been checked, the oil is washed with water or acid and the fat is subsequently bleached as usual.

Fig. 7 is a flow diagram of a continuous interesterification plant: The neutralised and washed fat blend is heated to 120°C by means of a heat exchanger and dried in two stages by spraying it into a vacuum. With the water content of the fat below 0.01% , a quantity of sodium (0.04 to 0.08% of the fat volume) is added as catalyst and then finely dispersed with a homogeniser. After passing through a sojourn section the catalyst is broken down and the hydrogen produced is drawn off. The interesterified mixture of fats is cooled to 95°C , washed with water, and separated from the aqueous phase in a centrifuge. When it has passed through a further vacuum-drying stage the fat passes on to the usual sequence of reactions, starting with bleaching. These plants have a capacity of 5 to 15 tons per hour, and the reaction time is 2-4 minutes.

Fig. 8 is a flow diagram of a plant patented by Procter & Gamble for continuous directed interesterification of lard: The lard is first heated to 150 to 170°C and dried by spraying it into a vacuum of 15 Torr

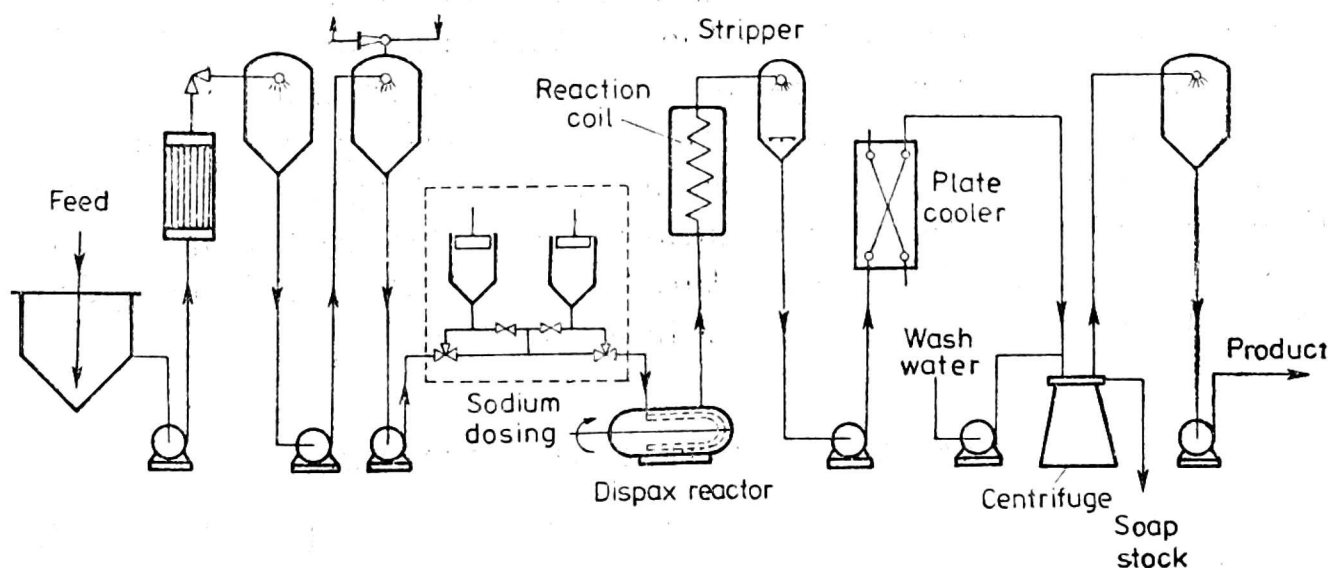


Fig. 7. Continuous interesterification plant using sodium as catalyst

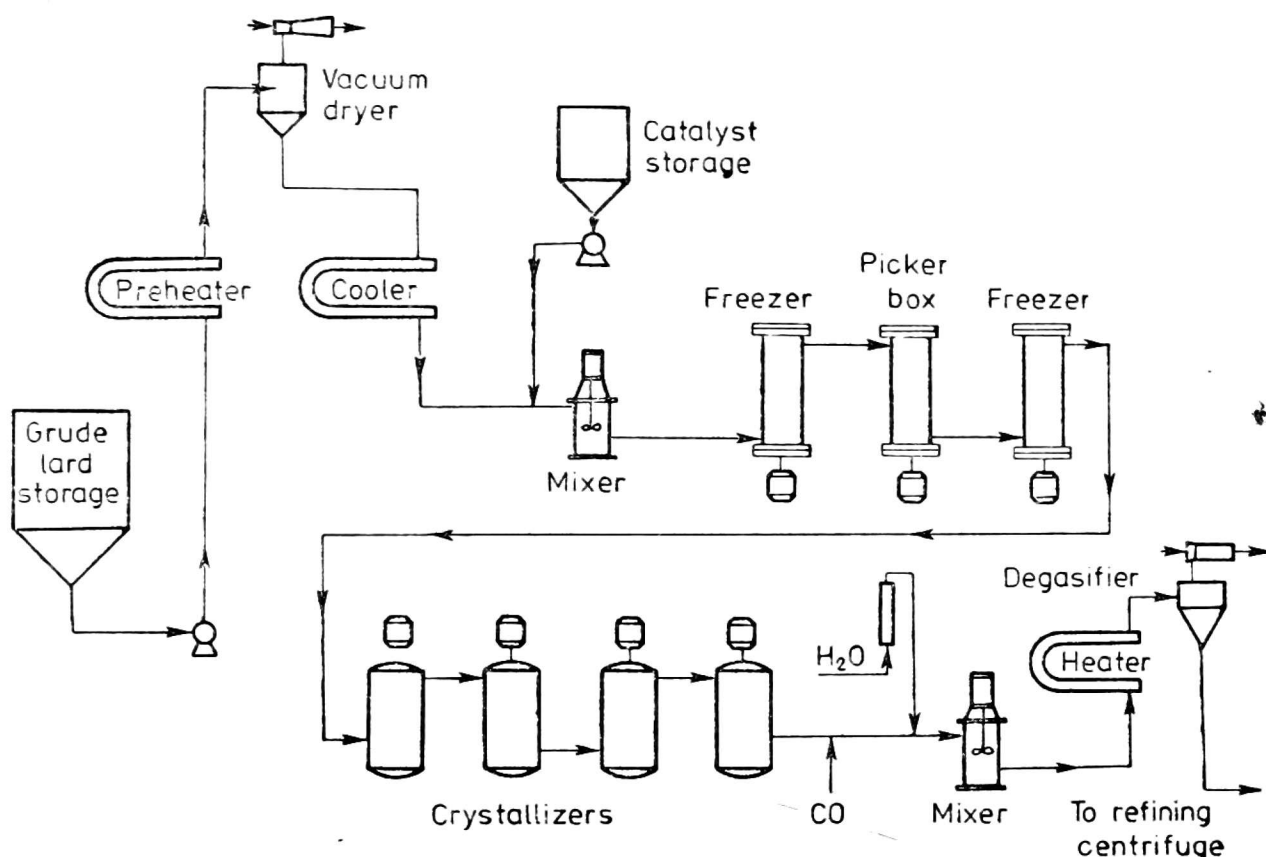


Fig. 8. Plant for continuous directed interesterification (Procter and Gamble).
After [3]

(approx. 0.29 psig). It is then cooled to 40°C , at which point 0.2% (of the fat quantity) of a liquid sodium-potassium alloy is added and finely dispersed by means of a homogeniser. Undirected interesterification at 40°C reached equilibrium in approx. 6 minutes.

Before the undirected interesterification can reach completion, the mixture is cooled to approx. 21°C in ammonia-cooled votators, causing crystal nuclei of trisaturated glycerides to form. It then passes to a working vessel in which these nuclei grow into stable crystals. At the same time the latent heat of solidification which is liberated raises the temperature to approx. 28°C , so the mixture is again cooled to 21°C in a votator. This is followed by an extended crystallisation phase lasting some 90 minutes, which takes place in large crystallisation vessels under constant stirring. The reaction is stopped by adding water and CO_2 when the proportion of trisaturated glycerides reaches approx. 14%. After a through mixing the mixture is heated, the resulting hydrogen exhausted and the water separated in a centrifuge.

ANALYSIS OF INTERESTERIFICATION

There are a large number of methods for investigating the results of interesterification. Like the dilatation curve, most of the other methods are based on the fact that interesterification causes a shift in the ratio

of solid to liquid glycerides. They include measurement of the melting point, cloud point, the slip point and the refractive index of the melt, as well as plotting a cooling curve (Fig. 9) or performing a differential thermoanalysis (Fig. 10).

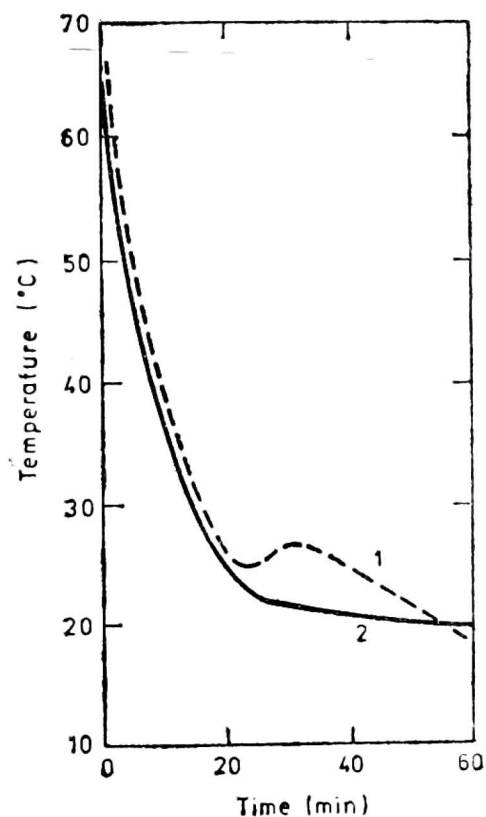


Fig. 9. Cooling curves of lard. After [8]

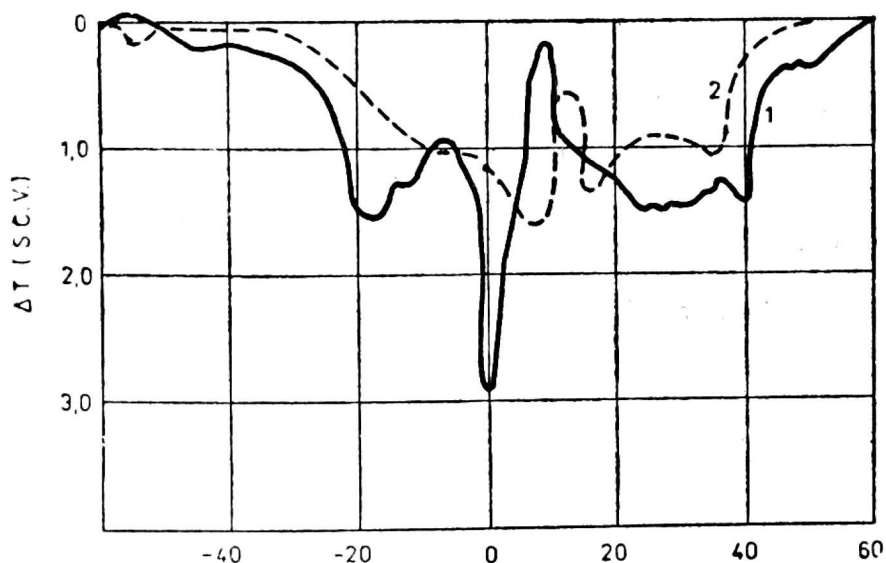


Fig. 10. DTA cooling curves. After [8]

However, with all these methods one requires for comparison a sample of the substance as it was before interesterification, though this does not as a rule pose any problems. Independently of such indirectly determined data and at the same time independently of the blend involved, the presence of free sterols permits reliable conclusions to be drawn about the results of interesterification, since the esterification

of free sterols runs strictly parallel with interesterification. However, this analysis is not exactly easy to perform and despite excellent results in the laboratory has therefore failed to establish itself as a straightforward test in the factory.

The results of randomisation can likewise only be investigated by means of highly complicated methods. The best of these has proved to be triglyceride analysis by gas chromatography, especially since for comparison purpose one can statistically calculate the new distribution of the fatty acids which should result from interesterification (Fig. 11).

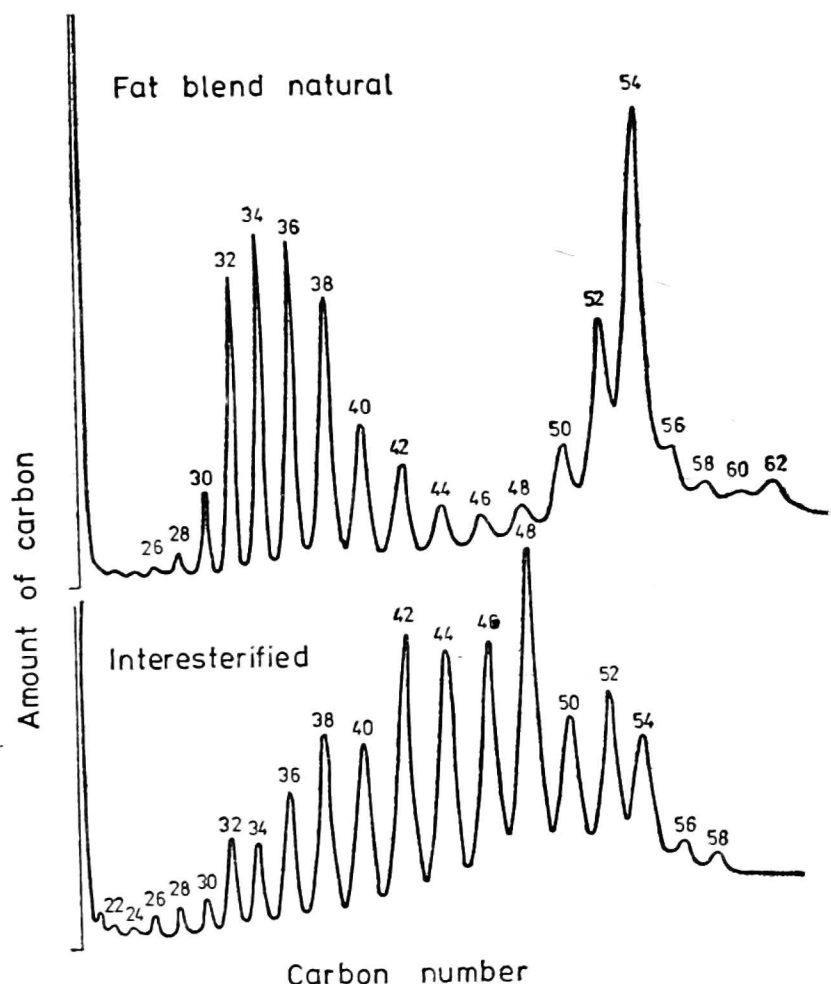


Fig. 11. GLC — distribution of triglycerides. After [8]

APPLICATIONS OF INTERESTERIFICATION

The interesterification process is widely used in the fat-processing industry, and we can conveniently distinguish four groups on the basis of the fats and interesterification processes used:

- a) undirected interesterification of straight fats,
- b) directed interesterification of straight fats,
- c) undirected interesterification of fat mixtures,

d) directed interesterification of fat mixtures.
Let us examine some examples of each.

EXAMPLES

a) One of the most important applications of the undirected interesterification of straight fats, practised abroad for decades now, is the treating of lard, a fat which in its untreated state has properties which produce undesirable results, especially when the fat is used for baking: it is difficult to cream, is a poor shortener, and compares with hardened vegetable fats it results in baked goods of insufficient volume. The rea-

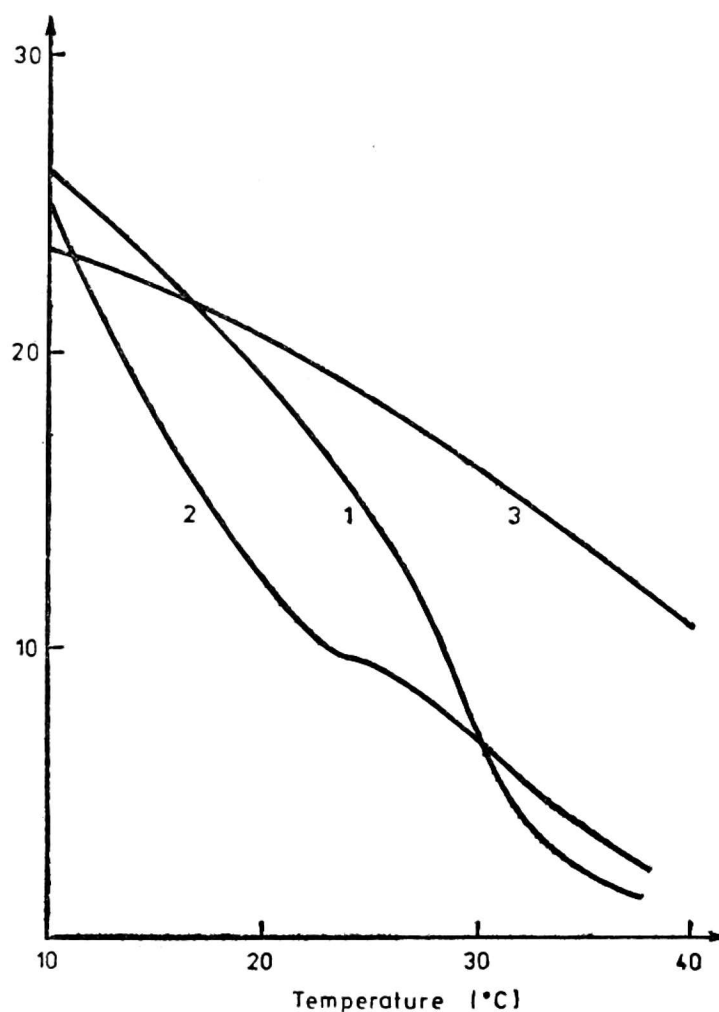


Fig. 12. Solids-lines for lard. After [3]

son for this lies in the abnormal structure of some of its triglycerides, in which palmitic acid occupies the β -position. Undirected interesterification eliminates these undesirable properties, giving lard the same high practical value as hardened vegetable fats (Fig. 12).

b) Directed interesterification can be used to produce a variety of fats for different uses. For example, one can obtain from cottonseed oil semi-solid fats suitable for use as baking fats. Sunflowerseed oil and

safflower oil yield soft plastic fats suitable for production of margarine with a high linoleic acid content.

This process produces in palm oil and hydrogenated fats an increase in the proportion of those solid components, in the form of saturated and monounsaturated which are capable of separation by fractionation. The solid fractions can be put to a variety of uses, the liquid fractions are notable for their high degree of resistance to oxidation as compared with natural liquid vegetable oils and are suitable for use as deep-frying oils etc.

c) The group of fat mixtures subjected to undirected interesterification is the most important one from a technological point of view. These mixtures of fats often form a large, if variable, proportion of the blends used in the manufacture of cooking fats and margarine.

Let us take a few examples:

— The interesterified blend may consist of partially and selectively hydrogenated fat on the one hand and vegetable oil on the other. In addition to a whole range of commonly available margarines this group includes the special cases of those margarines which are made from a single variety of oil, e. g. sunflowerseed oil.

— The interesterified blend may consist roughly of two-thirds palm oil and one third palm kernel fat or coconut fat (Fig. 13).

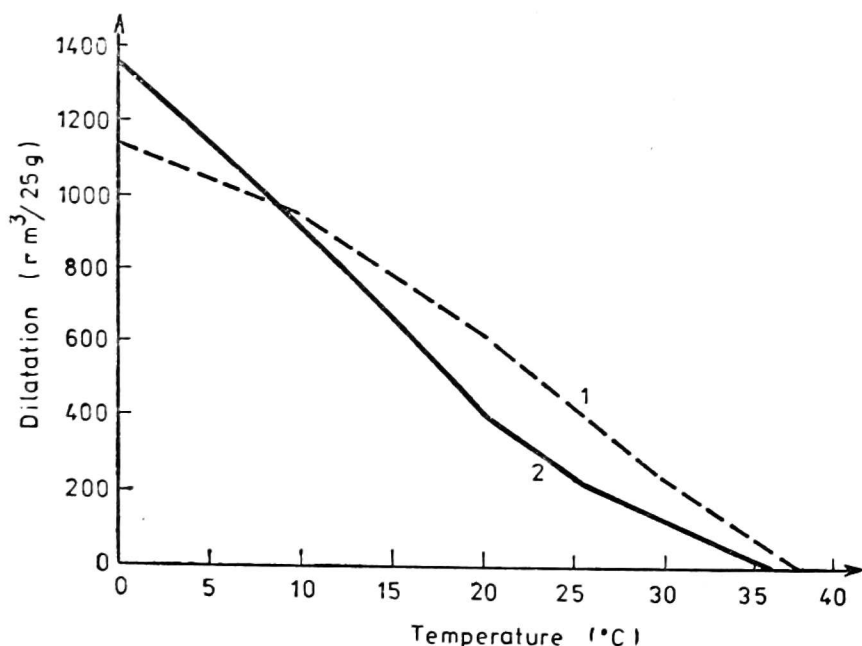


Fig. 13. Dilatation lines for palm oil/palmkernel mixture. Handbuch der Lebensmittelwerke Vol. IV p. 238, published by L. Acker *et al.* Springer-Verlag 1969

— The interesterified blend may consist of fully hydrogenated vegetable fat and linoleic-acid rich vegetable oil. These interesterified blends are used for margarine rich in linoleic acid.

— The interesterified blend consists of tallow and consistent fats or oils, resulting in a cooking fat or margarine with far more acceptable melting properties.

d) Directed interesterification is confined as a rule to straight fats, and has so far been little used for mixtures. In principle, however, the choice of source materials is very largely a free one. Nevertheless, the long reaction time required at the low reaction temperatures (many hours or even days at $T < 30^{\circ}\text{C}$) is a major deterrent to its widespread adoption in industry.

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PRZEESTRYFIKOWANIE JAKO METODA OTRZYMYWANIA OKREŚLONYCH TŁUSZCZÓW JADALNYCH

Streszczenie

Przez ostatnie 30 lat przeestryfikowanie olejów i tłuszczów uzyskało prawie podobne znaczenie, jak uwodornienie miało poprzednio. Porównując oba procesy, przeestryfikowanie wymaga mniejszych inwestycji i kwalifikacji niż uwodornienie. Skuteczna i szybka kontrola przeestryfikowania jest wciąż drugorzędnym problemem i jest przeprowadzana za pomocą metod pośrednich.

Razem z uwodornieniem i frakcjonowaniem, przeestryfikowanie jest wartościowym narzędziem do otrzymywania praktycznie nieograniczonej ilości mieszanek tłuszczu dla przemysłu tłuszczów jadalnych. Tłuszcze, które przedtem miały ograniczony stopień stosowalności, obecnie mogą być używane łatwiej dzięki przeestryfikowaniu. Odnosi się to szczególnie do wysokotopliwych tłuszczów, takich jak łój wołowy, frakcje oleju palmowego lub oleje, które muszą być uwodornione do wysokich temperatur topnienia w celu polepszenia trwałości.

Specjalne tłuszcze, jak margaryna, z wysoką zawartością kwasu linolowego, kompozycje tłuszczów nie zawierających izomerów trans lub miękkie margaryny i tłuszcze do smażenia nie byłyby możliwe do uzyskania bez przeestryfikowania — chociażby ze względu na wysokie koszty.

Tak więc przeestryfikowanie przyczyniło się w całej rozciągłości do wykorzystania światowych zasobów tłuszczu bardziej ekonomicznie i elastycznie.

К. Ф. Гандер

ПЕРЕЭТЕРИФИКАЦИЯ КАК МЕТОД ПОЛУЧЕНИЯ ОПРЕДЕЛЕННЫХ СЪЕДОБНЫХ ЖИРОВ

Резюме

В течение последнего 30-летия переэтерификация масел и жиров приобрела почти такое же значение, какое прежде имела гидратация. Сравнение обоих процессов показывает, что переэтерификация требует меньших затрат и квалификаций, чем гидратация. Эффективная и быстрая проверка переэтерификации является все еще второстепенной проблемой и проводится с помощью косвенных методов.

Наряду с гидратацией и фракционированием, переэтерификация является ценным способом получения практически неограниченного количества жирных смесей для промышленности съедобных жиров. Жиры, которые раньше использовались в ограниченном масштабе, в настоящее время могут использоваться более широко благодаря переэтерификации. Это касается особенно высокоплавных жиров, таких как говяжье сало, фракции пальчого масла или масел, которые необходимо гидратировать до высоких температур таяния с целью улучшения их прочности.

Специальные жиры, такие как маргарин, с высоким содержанием линолевой кислоты, композиции жиров без содержания транс-изомеров, или мягкие маргарины и жиры для поджаривания, не были бы возможными для производства без переэтерификации, хотя бы из-за высокой стоимости.

Таким образом, переэтерификация способствовала в значительной степени более экономному и эластичному использованию мировых ресурсов жиров.