SCI LECTURE PAPERS
SERIES

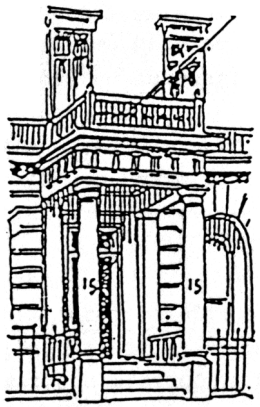
PAPER No 0039

ISSN 1353-114X

Timms RE

PRINCIPLES OF FAT FRACTIONATION

From the Oils & Fats Group symposium *Fractional Crystallisation of Fats* held in London on 9 March 1994



PRINCIPLES OF FRACTIONATION

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ABSTRACT

The purpose of fractionation is to separate a fat into two or more fractions distinguishable by their physical and chemical properties. Ideally, each triglyceride would be separated completely into a single fraction. In practice, this ideal is not possible due to (a) mutual solubility of one triglyceride in another leading to the formation of solid solutions, (b) physical difficulties in the separation of the liquid fraction from the solid, crystalline, fraction.

The principles of phase behaviour and the formation of solid solutions are briefly explained. These principles are then applied to the fractionation of palm oil to remove trisaturated triglycerides (mainly tripalmitin, PPP) as a solid fraction. It is shown that it is theoretically impossible to produce pure PPP.

After crystallisation, crystals are separated by filtration or centrifugation. The retention of the liquid fraction by the solid crystalline fraction is called entrainment and is quite separate and distinguishable from the formation of solid solutions. The theoretical range of entrainment in fat crystallisation is discussed and compared with practical results for different separation methods.

PRINCIPLES OF FRACTIONATION

The purpose of fractionation is to separate a fat into two or more fractions distinguishable by their physical and chemical properties. Ideally, each triglyceride would be separated completely into a single fraction. In practice, this ideal is not possible.

To illustrate my paper I shall use examples and data from the fractionation of palm oil, but the principles apply equally to other fats which are fractionated.

The triglyceride composition of palm oil and olein are shown in Table 1. It can be seen that the fractionation of palm oil to produce a more liquid olein fraction consists essentially of removing the trisaturated triglycerides. Since there is 8% trisaturated triglycerides in the oil and 7½% has been removed by fractionation, we might expect to have a stearin yield of about 8%. In practice for dry fractionation, yields of stearin are 20-35% depending on the process. Even using a solvent, a yield of 7½% is not achievable. The reasons for this large difference between the practical and the desirable are:

(a) mutual solubility of one triglyceride in another leading to the formation of solid solutions;

(b) physical trapping or entrainment of the liquid fraction by the solid, crystalline, fraction.

In this paper I shall briefly consider each of these reasons.

Solid Solutions

When a fat is cooled, a solid phase will eventually separate whose composition and amount depend principally on the temperature. The situation is illustrated schematically in Figure 1 which shows the phase diagram of a binary mixture of triglycerides A and B which form a continuous solid solution*.

* A solid solution is a mixture in which there is only one phase and one crystal form or polymorph. The components of the solid solution are not physically distinguishable, just as the components of a liquid solution are not distinguishable.

Holding the mixture at a temperature T_1 results in the formation of a solid phase of composition c in a liquid of composition a. The percentage of solid phase is (ab/ac) x 100.

From the phase diagram we can see that there is no temperature at which pure B can be crystallised from a mixture of A and B.

Now consider the real phase diagram shown in Figure 2 of the triglycerides PPP and POP, the principal triglycerides which crystallise during the fractionation of palm oil. The phase diagram shows that POP forms a solid solution with PPP and at temperatures below 30C about a third of the solid solution is POP. Thus if we wish to remove 8% PPP from palm oil then we should expect to crystallise a fraction in about 12% yield containing 8% PPP and 4% POP. In practice, there are other triglycerides in palm oil, but they do not substantially disturb the picture given by this phase diagram.

A phase diagram describes an equlibrium state. In the industrial fractionation of fats time is often not allowed for equilibrium to be achieved. In that situation the formation of solid solutions will be more extensive and poorer separations will result.

Laboratory fractionation results, using a solvent and with extensive washing of the filtered crystals, confirm these conclusions. The best stearin fractions that can be obtained which remove substantially all the PPP always contain at least 25% POP.

Entrainment

The basic fractionation step in the palm oil fractionation industry is a single fractional crystallisation process to remove a stearin and an olein with Iodine Value of 56-58 and Melting Point of 20-22C. There are several processes in use. All produce the same olein but very different stearins in different yields (Table 2).

In general it is true to say that it is the separation stage that determines the properties of the stearin, although the preceding crystallisation may affect the efficiency of separation that can

be achieved with a given separation technique. The difference between a so-called soft stearin with IV of about 45 and a hard stearin with IV of 30-35 or even less, is not to be found in the composition of the solid phase itself - that has been determined by phase principles and solid solution formation - but in the amount of mother liquor (olein) trapped or entrained in the separated crystals.

Entrainment is due to the three-dimensional structure of the aggregated crystals. The crystals have fissures where liquid is held by capillary and viscous forces. Entrainment is quite distinct from the formation of solid solutions.

How much olein is entrained in the stearins from the various process?

We can write:

$$S = E + C$$

$$S \cdot IV^s = C \cdot IV^c + E \cdot IV^o$$

where S = % of stearin in oil
C = % of crystals in oil
E = Entrainment = liquid(olein) trapped in the crystals, expressed as a percentage of the stearin
IV^o, IV^s, IV^c are the Iodine Values of olein, stearin and crystals

Combining and rearranging the equations:

$$IV^o - IV^s = \frac{1}{S} \cdot C \cdot (IV^o - IV^c)$$

Thus if $(IV^o - IV^s)$ is plotted against 1/S, we should obtain a straight line. In Figure 3, the data from Table 2 is plotted and it can be seen that a reasonable fit to the equation is found. Indeed, the fit is considered good considering that the palm oils used in the various processes were not the same and the crystallisation conditions were all different.

The slope of the line in Figure 3 is 5.3. If we take IV^c as 8 (the lowest value we can get with crystallisation from solvent plus washing of the crystals) then we can calculate C, the absolute amount of crystals in the oil. $[C \cdot (IV^o - IV^c) = 5.3]$ The result is, C = 0.106. In other words, 10.6% is the best possible stearin yield (0% entrainment) that could be obtained when an olein of IV 56-58 is produced.

Using this value of 10.6% the results for entrained oil given in Table 3 have been calculated. These results are in good agreement with Hamm's calculations [Fette Seifen Anstrichm. 1986 88 533-7].

Membrane or pressure filtration has clearly decreased the amount of oil entrained in the stearin. Yet even in this case entrainment is still surprisingly large and there is still considerable scope for improvement. In theory it might be imagined that by increasing the pressure to some high value all the entrained oil could be squeezed out. Indeed, we shall hear later about equipment that can increase the pressure and reduce entrained oil further. In practice a limit is always reached due to the structure of the crystals and some olein is always trapped in the press cake.

There is often surprise at the high levels of olein entrained in the apparently dry stearin cake. With NMR measurement of solid fat content now commonplace, it is easy to confirm the accuracy of the figures in Table 3. In Table 4, some figures for a laboratory crystallisation and filtration of palm oil are shown. The results are in excellent agreement with the conclusions in this section.

To Conclude

It is not possible to get a pure triglyceride fraction by cooling a molten fat and separating the crystals. Relatively little can be done about the formation of solid solutions, but there is much scope for improved physical separation of crystals from the oil. During the rest of the day we shall hear details of how the problems I have highlighted are mimimised in practice.

TABLE 1. COMPOSITION OF PALM OIL & OLEIN

TRIGLYCERIDE	OIL	OLEIN
SSS (mainly PPP)	8	½
S_2U (mainly POP)	50	48
SU_2 (mainly POO)	37	44½
UUU	5	7
Iodine Value	51-53	57-58

S=saturated, U=unsaturated fatty acid
(from Deffense)

TABLE 2. PALM STEARIN YIELDS & IODINE VALUES
FOR DIFFERENT FRACTIONATION PROCESSES

COMPANY	PROCESS	YIELD	IV
Alfa Laval	Detergent	17-23	25-35
Tirtiaux	Dry + Belt Filter	28-33	29-40
De Smet	Dry + Drum Filter	37-40	45-47
Bernadini	Hexane	37-40	44-46
De Smet	Dry + Membrane Filter	20-21	32-33

(from De Smet & Tirtiaux(Deffense))

TABLE 3. ESTIMATES OF ENTRAINED OIL IN STEARIN
FROM DIFFERENT FRACTIONATION PROCESSES

COMPANY	PROCESS	YIELD	ENTRAINED OIL AS % STEARIN
Alfa Laval	Detergent	17-23	35-52
Tirtiaux	Dry + Belt Filter	28-33	60-67
De Smet	Dry + Drum Filter	37-40	70-73
Bernadini	Hexane	37-40	70-73
De Smet	Dry + Membrane Filter	20-21	47-50

TABLE 4. LABORATORY RESULTS
CRUDE PALM OIL CRYSTALLISED AT 22C
FILTERED ON VACUUM FILTER

FRACTION	YIELD	IODINE VALUE	SFC(%) @ 22C
Palm Oil		52.3	9.7
Stearin	31.5	43.9	29.4
Olein	68.5	56.2	0

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FIGURE 1. SCHEMATIC PHASE DIAGRAM OF TWO TRIGLYCERIDES A & B WHICH FORM A CONTINUOUS SOLID SOLUTION

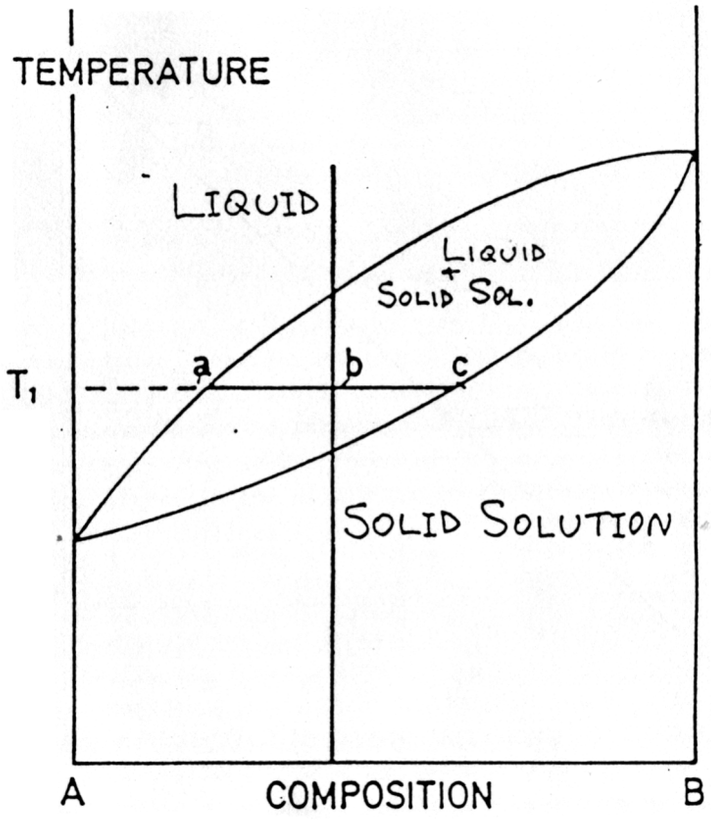

FIGURE PHASE DIAGRAM OF TRIPALMITIN(PPP) & 2-OLEO-DIPALMITIN(POP)

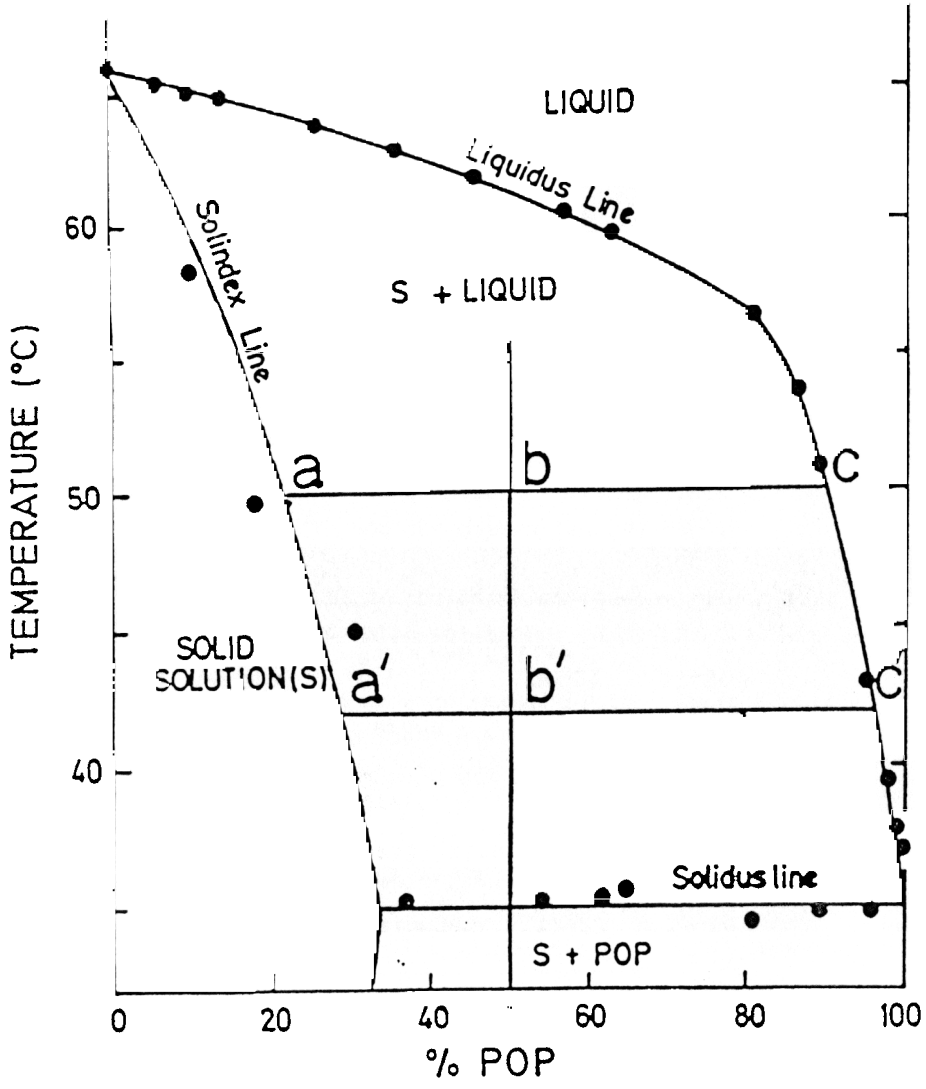

FIGURE 3. PLOT OF PALM OLEIN FRACTIONATION RESULTS ACCORDING TO ENTRAINMENT EQUATION (SEE TEXT)