STKM 2622: Advanced Chemical Analysis of Food Laboratory

Determination of Solid Fat Content (SFC) in Oils and Fats by pulsed-NMR Analyzer

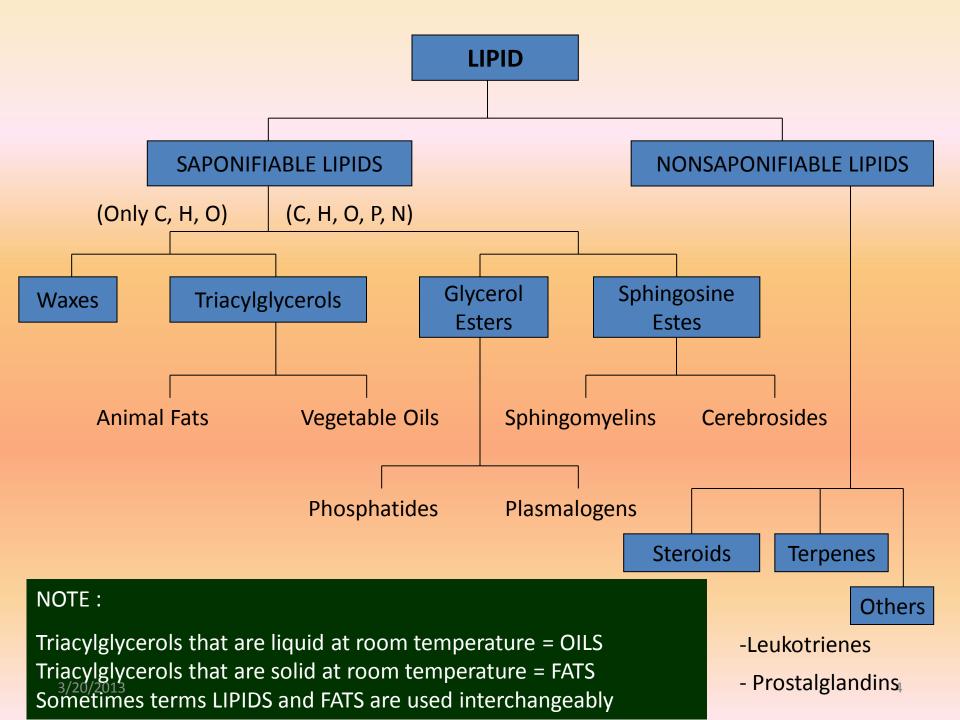
Assoc Prof Dr Nazaruddin Ramli School of Chemical Sciences & Food Technology FST, UKM

Introduction

Lipid

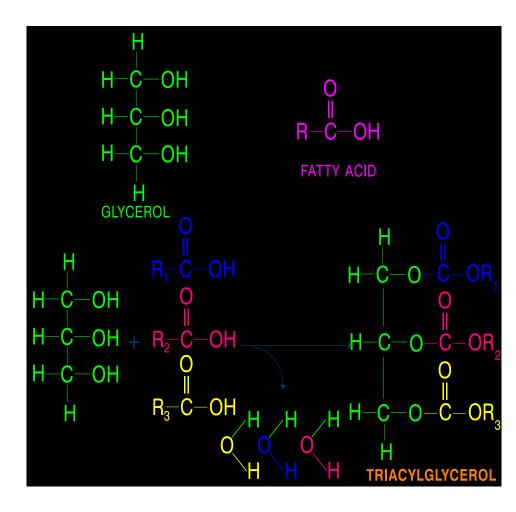
What is a *lipid* ?

- organic compounds soluble in non-polar solvent and insoluble in water
- formed from hydrocarbon backbone
- constitutes
 - triacylglycerols (fats and oils)
 - phospholipids
 - sterols
 - lipo-protein
 - fat-soluble vitamins

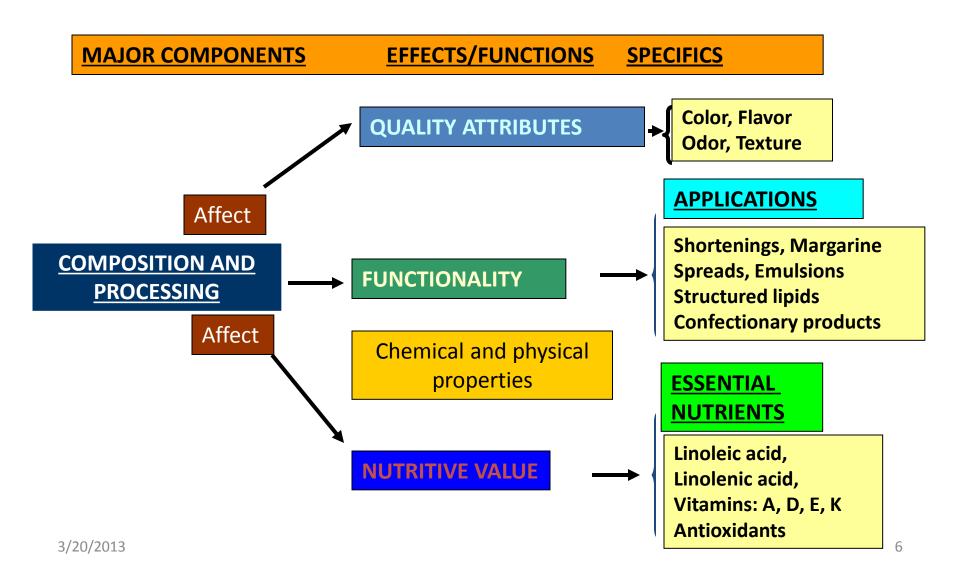


Fats and Oils

- Fats are solid at room temperature
- Oils are liquid at room temperature
- made of 2 components
 = glycerol + 3 fatty acids



Effect of Lipid Composition and Processing on Functionality of Foods



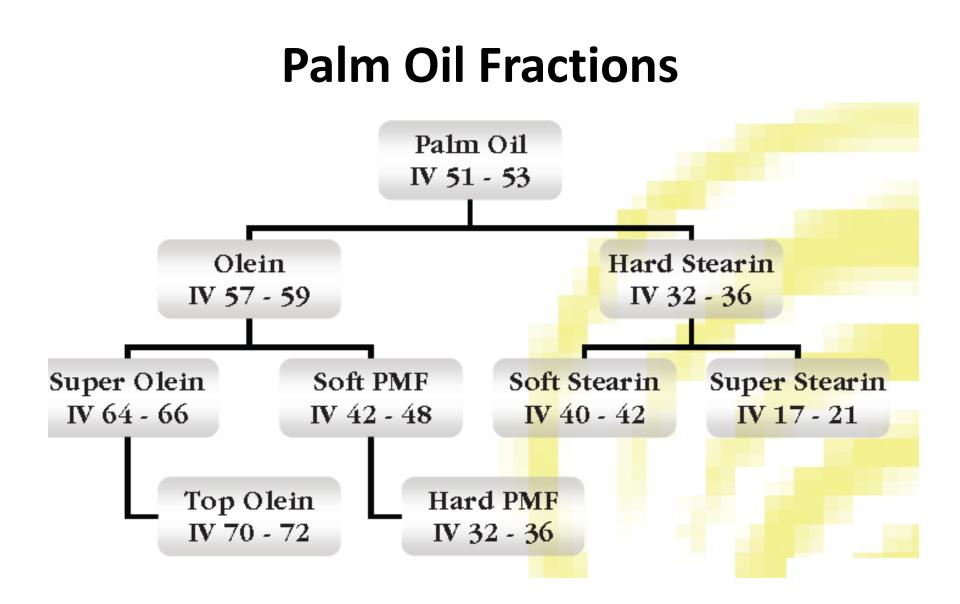
Oils and fats application

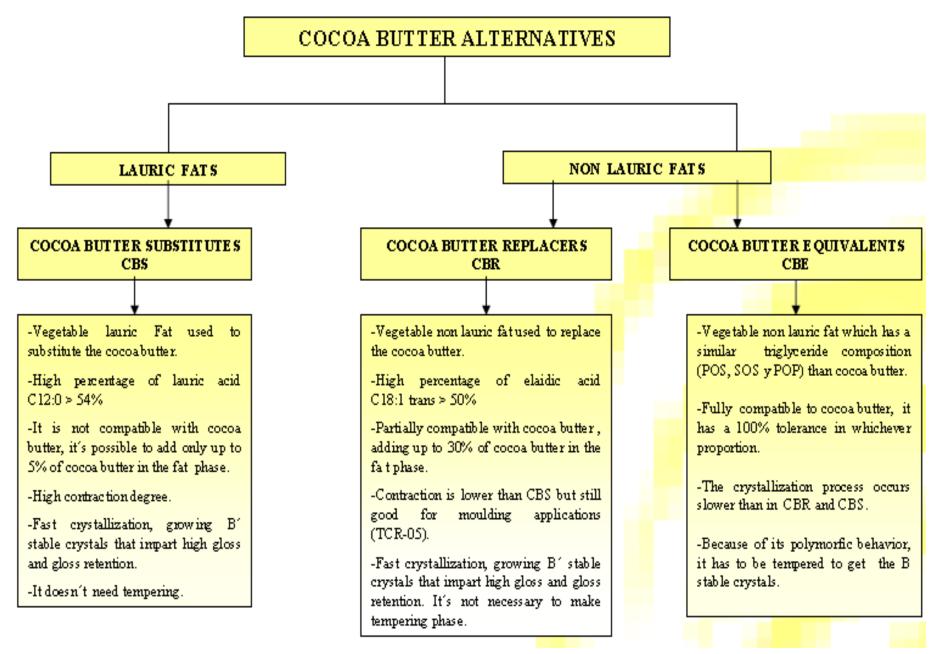
- Food (shortenings, frying, salad etc)
- Pharmaceutical
- Animal feed
- Biodiesel
- Cosmetic
- Lubricant
- Oleochemical

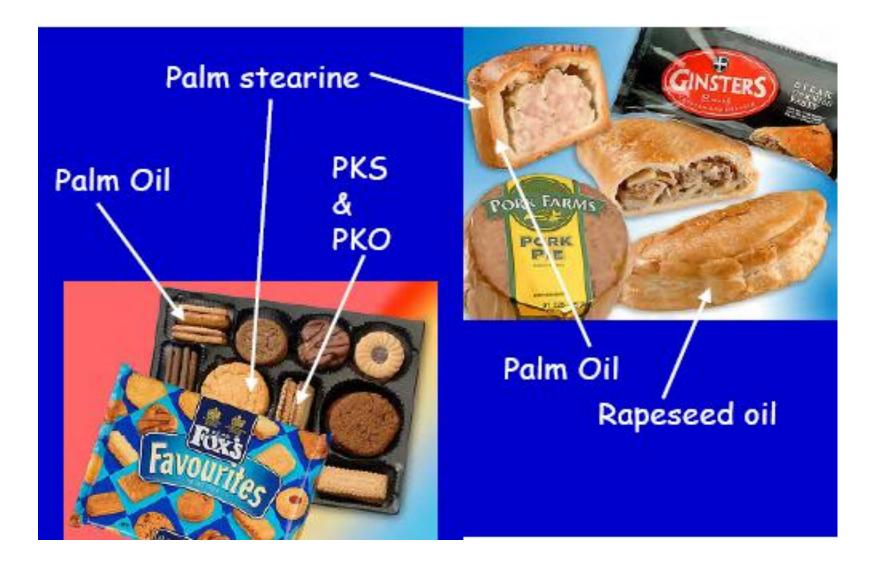


Food Products with Palm Oil









Physicochemical characteristics of fat and oils

- physicochemical properties:
 - such as mouth feel
 - flavor
 - texture
 - appearance
- analytical techniques
 - Solid Fat Content
 - Melting point
 - Cloud point
 - Smoke, Flash and Fire Points
 - Rheology

Application of Pulsed-Nuclear Magnetic Resonance (p-NMR) from Bruker

Determination of Solid Fat Content by Benchtop NMR is an internationally accepted procedure and an important analysis for producers and users of fats and oils in the food industry



Application: Food and Non Food

- 1. Determination of Solid Fat Content (SFC) and melt profile of fat compositions and margarines
- 2. Moisture content in margarine
- 3. Determination of polar parts in deep-frying oils
- 4. Oil or fat content in foods, confectionery products, and animal feeds
- 5. Simultaneous determination of oil and moisture in oilseeds
- 6. Fat and Moisture in milk powders and milk powder products
- 7. Moisture determinations in rice and a variety of foods
- 8. Total oil and/or moisture in emulsions
- 9. Water distribution in dispersions and gels
- 10. Droplet size distribution in water in oil emulsions
- 11. Investigation of freezing processes
- 12. Unilever water droplet size application (released)
- 13. Total Casein content in Milk





Polymer Applications

- 1. Density of Polyethylene
- 2. Changes in cross-link density
- 3. Finish or oil on natural fibers, yarns, and synthetic fibers
- 4. Xylene solubles in Polypropylene
- 5. R21-values of polypropylene
- 6. Plasticizers or elastomers in polymers
- 7. Rubber content in polymer blends
- 8. Copolymer ratios
- 9. Solid content of rubber latex
- 10. Glass in nylon
- 11. Monitoring of polymerization reactions
- 12. Viscosity measurements on polymerization reaction mixtures
- 13. Total fluorine analysis in polymers
- 14. Fluorine-finish on fibres



Pharmaceutical Applications

- 1. Moisture in powders (free and bound)
- 2. Moisture in catalysts
- 3. Oil or liquids in solid matrices or powdered chemicals
- 4. Diffusion of liquids in liquids, powders, rock cores, zeolites and other hosts
- 5. Liquid or waxy coatings on solid particles
- 6. Viscosity of liquids
- 7. Determination of the extent of nitration of alcohols



SFC analyses

- Solid Fat Content (SFC)
- Solid Fat Index (SFI) Measurements

SFC

 The first version of an AOCS official method for SFC determination by low resolution NMR was published in 1993 (AOCS Official Method Cd 16b-93). Bruker has fully supported the NMR Committee and its work.

Official SFC Methods

- Solid Fat Content (SFC) is the generally accepted analysis of fats and oils in the food industry.
- SFC influence to sensory and physical properties, such as spread ability, firmness, mouth feel, processing and stability. *e.g.*, margarine and butter.
- The traditional methods for SFC determination are slow, irreproducible and require additional chemicals

SFC by NMR

- Solid Fat Content determination by NMR is based on direct ratio measurement between the solid and liquid parts of the sample observed in the NMR.
- is defined as the percentage of the total lipid that is solid at a particular temperature, *i.e.* $SFC = 100M_{solid}/M_{total}$, where M_{solid} is the mass of the lipid that is solid and M_{total} is the total mass of the lipid in the food.

Reference Method

- Direct measurements of SFC by NMR can be performed quickly and accurately. NMR as a method of analysis has been established by the following standards:
- Presently, the AOCS official methods are:
 - AOCS Cd 16b-93 revised in 2000; Direct Method
 - AOCS Cd 16-81 revised in 2000, Indirect Method
 - PORIM Test Method (1995)
- Official methods for SFC in Europe:
 - ISO 8292
 - IUPAC 2.150

A variety of methods of Solid Fat Content

- **density** of solid fat is higher than the density of liquid oil, so density increase when fat crystallizes and decrease when it melts determine the solid fat content temperature profile:
- The density is usually measured by density bottles or dilatometry.
- **NMR** quicker and simpler to carry out but expensive.
- differential scanning calorimetry (DSC) measure the heat evolved or absorbed by a lipid when it crystallizes or melts. By making these measurements over a range of temperatures it is possible to determine the melting point, the total amount of lipid involved in the transition and the SFC-temperature profile.

Advantages of p-NMR

- NMR is very accurate and reproducible
- Analyses take less time to complete than SFI determinations
- NMR yields a SFC value from a single measurement when the Direct Method is employed
- SFC procedure does not overly dependent on operator technique and judgement
- The procedure can be automated
- NMR can be used to obtain relative values for quality control even on finished products that contain water
- NMR is non-destructive; the same sample can be measured numerous times or used for other analytical tests.
- Approved AOCS methods

Solid Fat Index (SFI)

- Popular in US, traditional method used for measuring the solids content of edible oils by dilatometry
- SFI is an empirical value that is derived from expansion of a fat as a chilled sample is warmed. In the process of melting, previously crystallized parts of the sample become liquefied
- Dilatometry does not directly measure the solids content of fat at any given time, rather it measures the change in volume compared to the starting point.
- SFI measurements depend on consistent operator skill and judgement for accuracy and reproducibility.
- Leaky dilatometer burettes, bubble formation and other artifacts can ruin an entire series of SFI determinations.
- SFI values for fats that contain emulsifiers are not very accurate due to some dissolution of emulsifiers into the indicator at the fat/indicator boundry

Solid Fat Index

- SFI is an empirical value that is derived from expansion of a fat as a chilled sample is warmed.
- In the process of melting, previously crystallized parts of the sample become liquefied.
- Since the fat molecules in a liquid state are less efficiently arranged in space compared to closely packed crystalline regions, liquid fat takes up more volume.
- Therefore, the degree of expansion is related to the change in the solid content.

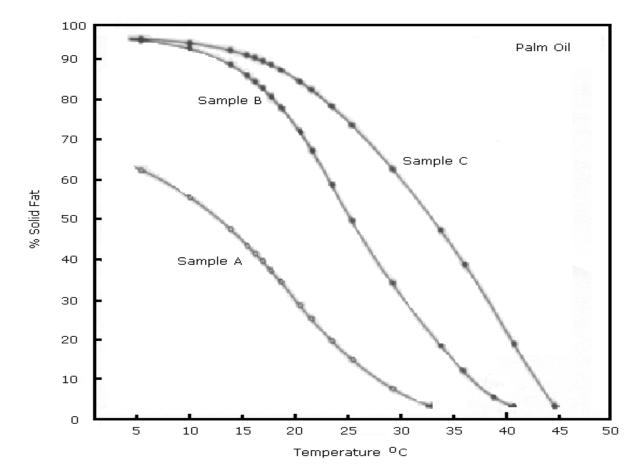
Disadvantages of SFI

- Dilatometry does not directly measure the solids content of fat at any given time, rather it measures the change in volume compared to the starting point.
- SFI measurements depend on consistent operator skill and judgment for accuracy and reproducibility.
- Leaky dilatometer burettes, bubble formation and other artifacts can ruin an entire series of SFI determinations.
- SFI values for fats that contain emulsifiers are not very accurate due to some dissolution of emulsifiers into the indicator at the fat/indicator boundry.
- A strong impetus therefore exists to adapt an alternative method.

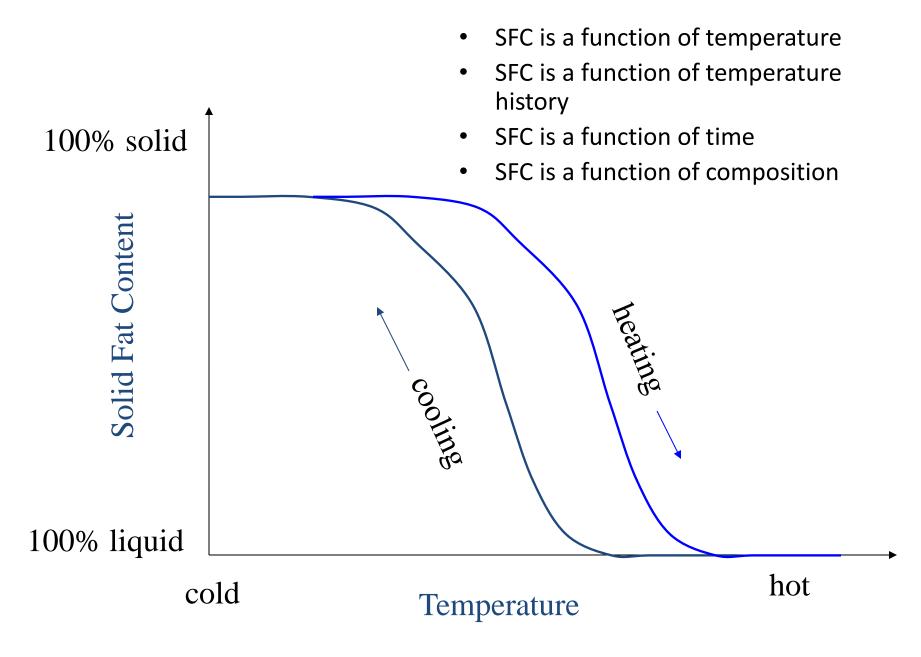
Interpretation

What we get from p-NMR?

• SFC profile



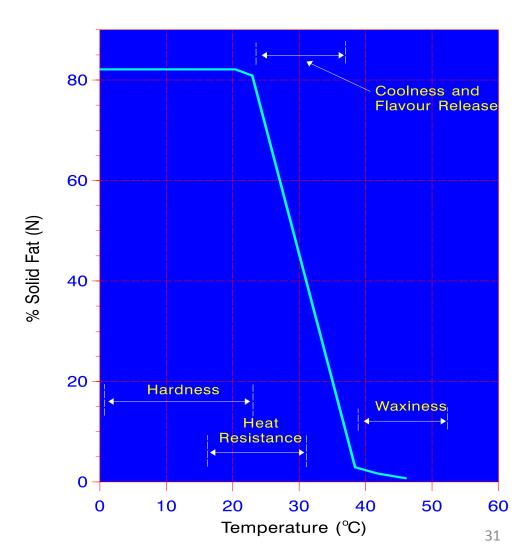
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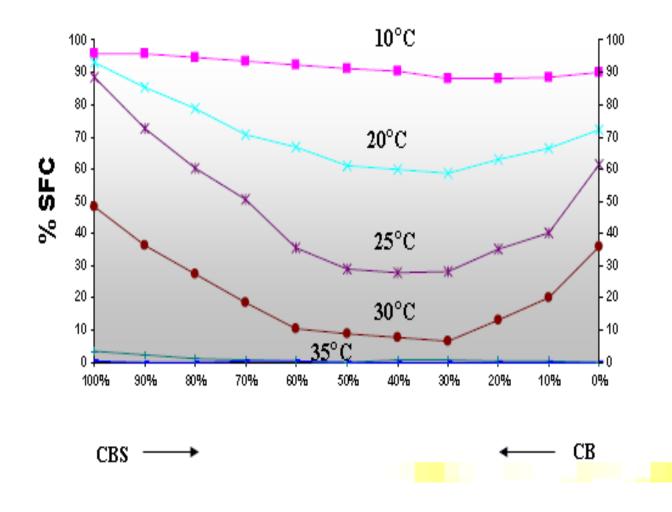
SFC in chocolate products

Vegetable fats

 (e.g. CB & CBA)
 in chocolate □
 hardness, heat
 resistant,
 mouthfeel &
 flavour release

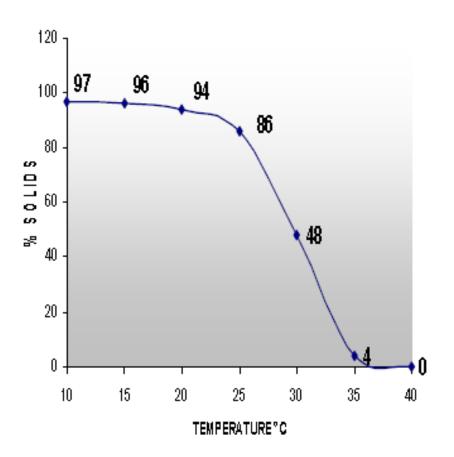


CBS Tolerance to Cocoa Butter

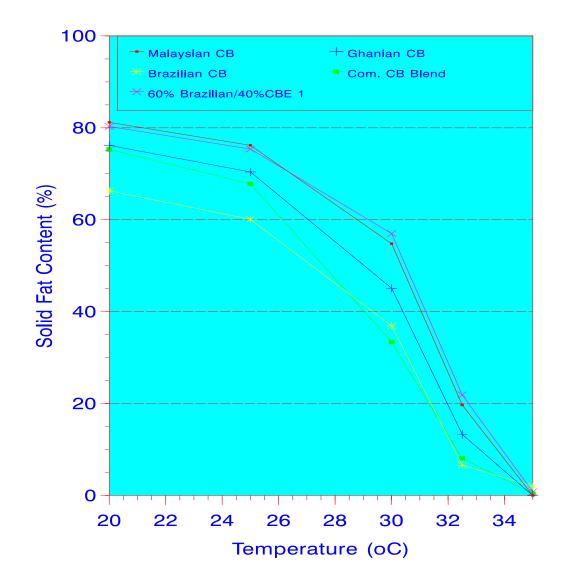


SFC profile for CBS

- Primarily used for molded products because its excellent gloss and snapping.
- Ideal for making compound chocolate.
- Can be used for enrobing and panning of hard centres.

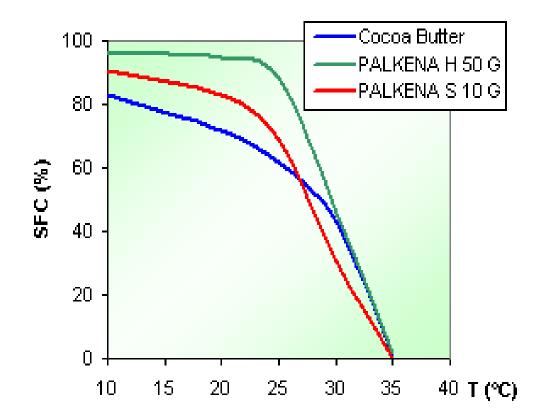


Modification of melting profiles of CBs (SFC)



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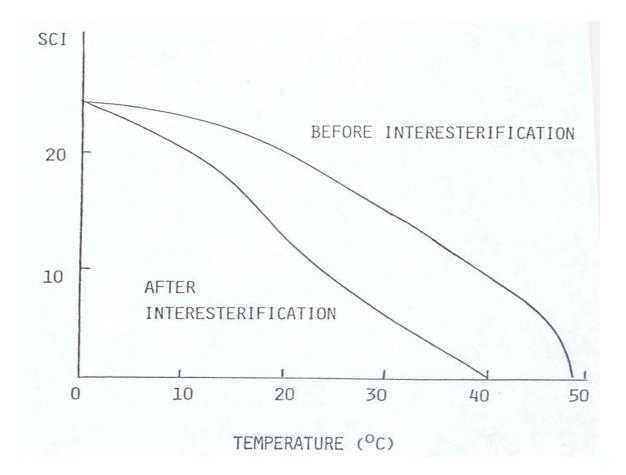
Cocoa Butter Replacer (CBR) from Fujioil, Jpn



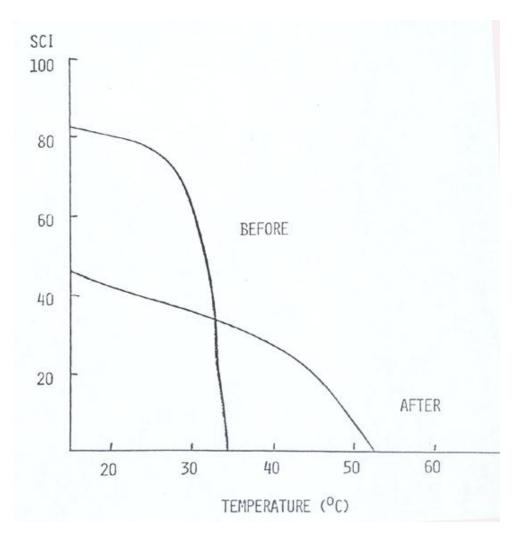
Confectionary Fats from Blend of Hydrogenated and Interesterified Hydrogenated Palm Kernel Oil

	SCI				
Fat	M.P.(°C)	10	20	35	38
Hydrogenated palm kernel oil (PKO)	46.8	74.2	67.0	15.4	11.7
Int. hydrogenated PKO	35.0	65.0	49.9	1.4	1.1
50% hydrogenated 50% int. hydrogenated	41.7	70.0	57.4	8.7	5.2

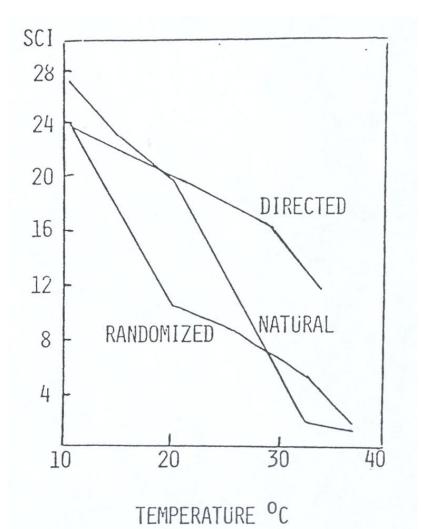
Effect of Randomization on SCI of an 80:20 Mixture of Lightly Hydrogenated Soybean Oil and Palm Stearine



Solid Content Index of Cocoa Butter before and after Interesterification



Changes in SCI of Lard by Interesterification



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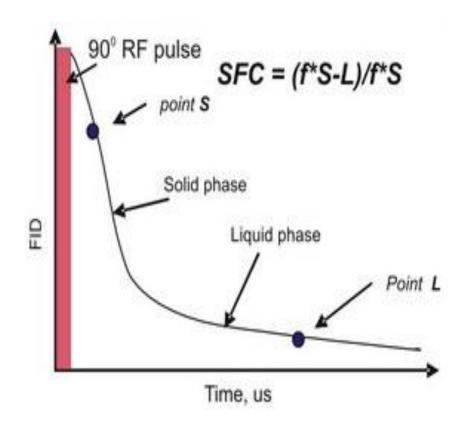
Principle

Solid Fat Content

- An SFC value is determined by detecting the NMR signal from both liquid and solid components in the fat sample, or by detecting the change in the liquid signal as it is displaced by solid.
- The minispec employs the "pulse" method to perform the NMR experiment. This means that a short intense burst of radio frequency (RF) energy is applied to the sample in the static magnetic field to cause excitation of the Hydrogen in the fat.

Principle of SFC Determination Using NMR

The SFC value is determined by taking two measurement points on the FID(Free Inducton Decay). FID amplitude at point S (corresponding to total solids plus liquids), and at point L (corresponding liquids only). The specific ratio can be found using equation shown on Fig. 1. This ratio is considered to be the SFC value.



Application Methodology for Direct Solid Fat Content Measurements

- The fat is melted at T = 80 to 100°C and held there for 15 minutes.
- The fat must be well-mixed prior to removing a representative and residue-free amount, which is used to fill a 10 mm diameter sample tubes to a height of 4 cm.
- Sample temperature is maintained at T = 60°C for at least 5 minutes but not more than 15 minutes.
- Transfer the sample to T = 0°C and maintain for 60 +/- 2 minutes (must be timed accurately).
- Transfer the sample to the temperature for which a measurement is needed. Maintain this temperature for 30 to 35 minutes (must be timed accurately).
- The creation of a melting curve requires the sample to be measured at many different temperatures (e.g. 10°C / 15°C / 20°C / 25°C / 30°C / 35°C etc).
- Insert the sample tube into the minispec for a 6 second analysis. The direct SFC method consists of the single measurement at the desired temperature. The direct parallel method consists of the consecutive measurement of solid fat content at all desired temperatures

Options for the SFC Measurement

- Two pulsed NMR methods exist for measuring the SFC of edible oils: the direct and the indirect methods.
 - The direct method measures the signal from both the solid and liquid components
 - The indirect method measures only the liquid signal and compares it to the signal from a fully melted sample.
- The direct method is very fast, reproducible and sample preparation is minimal. Melted oil is simply poured into an NMR tube to a height of approximately 4 to 5 cm and the sample is tempered in the tube. Only one NMR measurement is needed to obtain a SFC value by the direct method.
- The indirect method is also very reproducible and accurate and it is not as fast. More care must be taken when preparing samples. Four measurements must be performed at two temperatures in order to calculate the percentage of solids.

Apparatus

- Pulsed NMR Spectrometer (Bruker Minispec mq20)
- Circulating refrigerated water bath
- Reference sample for calibration (0%, 31.44%, 75.4%)
- Aluminum heating block

Sample preparation

- Sample must be melted (microwave or oven)
- Transferred to sample tube up to 3 cm but not more 4cm high
- Measured the ref sample
- Transfer the sample into 0C for 90min
- Then transfer all the samples simultaneously into circulating water bath
- After 30 min measure the SFC at specific temperature
- Normally: 0, 5, 10, 15, 20, 25, 30, 37, 40C

Melting



Preparation in sample tube



Incubation with different temperature





Calibration





SFC Measurement



















