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REFERENCIA : SOLICITUD DE REGISTRO DE LA PATENTE
**PRODUCTO GRASO SÓLIDO CON BAJO
CONTENIDO DE GRASA SATURADA Y LIBRE
DE ÁCIDOS GRASOS.**

EXPEDIENTE No. : 10-092087
CODIGO : 01-01-08

LAURA MICHELSEN NIÑO, mayor de edad, domiciliada en la ciudad de Bogotá D.C, República de Colombia, abogada titulada e identificada como aparece al pie de mi firma, me permito presentar éste memorial, en procura de proteger los intereses y derechos de propiedad intelectual de los empresarios y consumidores, en la medida que tal como será demostrado a continuación, la solicitud de patente de la referencia carece en su totalidad de nivel inventivo, y por ende no cumple con los requisitos de patentabilidad establecidos en el Artículo 14 de la Decisión 486 de la Comunidad Andina.

1. Consideraciones:

1.1 Conocimientos de una persona versada en la materia antes del 10 de enero de 2008

A continuación se resumen los conocimientos que, antes de enero de 2008, cualquier persona versada en la materia tenía sobre los ácidos grasos, los problemas relacionados con los trans isómeros y el uso del aceite de palma y sus fracciones como solución para reducir la cantidad de ácidos trans y elaborar grasas bajas en saturados útiles como ingredientes grasos para panadería, galletería, frituras, margarinas, esparcibles, etc.

La tendencia a preferir productos y grasas libres de trans y bajos en saturados no es nueva, ella está soportada en numerosos estudios epidemiológicos realizados desde los años ochenta¹, donde se relacionó el consumo de grasas trans y saturadas con consecuencias perjudiciales para la salud; en respuesta a esta los efectos adversos, las industrias de alimentos han trabajado en la búsqueda y generación de alternativas ampliamente documentadas, para obtener productos grasos sólidos, libres de trans y bajos en ácidos grasos saturados².

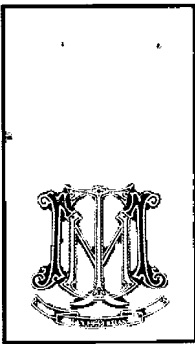
A la fecha, la alternativa más usual y básica para cumplir con las condiciones antes mencionadas es **la mezcla aceites insaturados - poli-insaturados con aceites saturados y/o con sus fracciones**^{3 4 5 6 7}, obteniendo un producto final que mantiene las ventajas

¹ 2008 – Cenipalma. “**Los ácidos grasos trans y la salud**”. Lípidos y Salud. Volumen 9. No.4 de 2008

² 2004 – G.R List. “**Decreasing Trans and Saturated Fatty Acid Content in Food Oils**” Food Technology. Vol 58, 2004. pp 23-31

³ 1998 - Petrauskaite V, De Greyt W, Kellens M, Huygebaert A. “**Physical and Chemical Properties of trans-Free Fats Produced by Chemical Interesterification of Vegetable Oil Blends**”. JAOCS. Vol. 75, No. 4 pp. 489-493

⁴ 2000 – Toro-Vazquez JF, Briceño-Montelongo M, Dibildox-Alvarado E, Charó-Alonso M, Reyes-Hernández J. “**Crystallization Kinetics of Palm Stearin in Blends with Sesame Oil**”. JAOCS. Vol. 77, No. 3 pp. 297-310



relacionadas con los aceites ricos en saturados como son: estabilidad, punto de fusión, libre de trans y con el contenido de sólidos requerido para la elaboración de margarinas, grasas para panificación y grasas para freír.

En la literatura anexa a este memorial, queda claro que dentro de los métodos más usuales para la reducción del contenido de grasas trans, muchas veces originadas por la hidrogenación parcial de los aceites insaturados, se encuentran las mezclas que comprenden aceite de palma, alguna de sus fracciones ^{2, 3, 4, 5, 6} y/o aceites de palma totalmente hidrogenado³.

Ahora bien, la mezcla es un método físico simple que no implica innovación ni uso de tecnología avanzada. En la industria de las grasas es bien sabido que *“la mezcla de aceites y grasas permite obtener productos finales con características propias. Ello podría ser considerado como un método de modificación física de aceites y grasas”*⁸. Así mismo, es conocido que del contenido de sólidos aportado por la parte saturada de la mezcla dependerán las características especiales de apariencia, plasticidad, etc, de la composición final.⁹

Por su parte, el aceite de palma crudo, en estado natural, es un sólido, sin ácidos trans y con alto contenido de saturados, que consiste en un 95% de una mezcla de triacilglicérol, que son moléculas de glicerol con punto de fusión de 34-40°C. El perfil del aceite de palma lo hace la materia prima ideal para remplazar las grasas hidrogenadas en formulaciones de grasas sólidas libres de trans, especiales para panificación, galletería, freído profundo, etc².

Los procesos de fraccionamiento e hidrogenación existen desde hace muchos años y en la actualidad son los equipos los que van evolucionando¹⁰. El proceso industrial de fraccionamiento del aceite de palma permite separar una fracción de bajo punto de fusión llamada oleína (líquida a 20°C), y una fracción sólida de alto punto de fusión llamada estearina^{7, 8, 11}, estas mismas fracciones se pueden fraccionar de nuevo, con esto se ha facilitado la producción de mezclas, incluidas combinaciones binarias de aceite de palma y su estearina en diferentes proporciones⁸.

Todos los aceites vegetales están compuestos de triglicéridos, que son triésteres de glicerol y de tres ácidos grasos, ver estructura básica a continuación:

⁵ 2003 – Kalyana Sundram, Ravigadevi Sambanthamurthi, Yew-Ai Tan. *“Palm fruit chemistry and nutrition”*. Asia Pacific J Clin Nutr 2003; 12(3) 355-362.

⁶ 2006 – Noor Lida HAbi Mat Dian, Kalyana Sundram, Nor Aini Idris. *“DSC Study on the Melting Properties of Palm Oil, Sunflower Oil, and Palm Kernel Olein Blends Before and After Chemical Interesterification”*. JAOCS Vo. 83, No. 8 pp. 739-

⁷ 2007 – Berger K.G. *“Trans-Free Fats with the Products of the Oil Palm – A Selective Review”*. Czech J. Food Sci. , 25: pp 174-181

⁸ 2008 – García D., Sandoval J., Saldaña R., Cárdenas G., Soplin J. Sotero V., Pavan R., Mancini J. *“Fraccionamiento e interesterificación del aceite de palma (Elaeis guineensis) cultivado en la Amazonía peruana”*. Grasas y Aceites 59 (2), Abril – Junio 104-109. 2008

⁹ 2003- Ihsan Karabulut, Semra Turan, Gürol Ergin. *“Effects of chemical interesterification on solid content and slip melting point of fat/oil blends”* Eur Food Technol (2004) 218:224-229

¹⁰ 2008 – Cenipalma. *“Modificación de aceites y grasas en la industria de alimentos”*. Lípidos y Salud. Volumen 9. No. 1 de 2008

¹¹ 1989 – Yap, PH, de Man, JM, de Man ,L. *“Polymorphism of palm oil and palm oil products”* Journal of the American Oil Chemists’ Society. 66(5) , pp 693-697



En el caso del aceite de palma, el ácido graso mayoritario es el **ácido palmítico (P)**, que ocupa principalmente las posiciones 1 y 3 de los triglicéridos, mientras la posición 2 está ocupada por **ácido oléico (O)** y **Linoléico (L)**. De esta forma el triacilglicerido mayoritario en el aceite de palma es **Palmítico–Oléico–Palmítico (POP)**¹² con un **28.7%**, seguido de **Palmítico–Oléico–Oléico (POO)** con un **23.7%** y en menor proporción con **Palmítico–Linoléico–Palmítico (PLP)** con un **11%** como se muestra en la tabla 1¹³. Así mismo, mediante el fraccionamiento de la estearina se puede obtener la **tripalmitina** que es un triacilglicérido compuesto de **Palmítico–Palmítico–Palmítico (PPP)**.

Tabla 1 Composición en triglicéridos del aceite de palma, según su grado de insaturación

Tipo de triglicérido	Estado físico a temp. ambiente	Aplicación	%*
SSS			
MPP		Producción de ácidos grasos	0,1
PPP			2,0
PPG	Sólido	Coberturas duras	0,7
PSS			0,6
SSS			0,2
SUS			
POP			28,7
POS	Semisólido	Chocolatería	4,2
SOS			0,2
PLP			11,0
SUU			
POO			23,7
SOO	Semilíquido	Margarinas	1,8
PLO			10,9
PLL			3,6
UUU OOO		Aceites para ensalada y para freír	3,3
OOL	Líquido		1,8
OLL			0,5
MG/DG			6,7

* Aceite de palma de Malasia

La tripalmitina es el triglicérido con la **más alta temperatura de fusión** tanto en el aceite de palma (con una concentración es de 5% a 10%) como en la estarina de palma (con una concentración de 12% a 56%), su inclusión en la formulación de grasas sólida también ha

¹² 2008 – Valenzuela, A. “Ácidos Grasos con Isomería Trans II. Situación de Consumo en Latinoamérica y Alternativas para su Sustitución” Revista Chilena de Nutrición. V.35 No. 3 Santiago Sep. 2008

¹³ 2004 – Cadena, AE. “Fraccionamiento en seco de los aceites de palma y palmiste y usos de las fracciones”. PALMAS Vol. 225 No. Especial, Tomo II, 2004. Pp 482-491



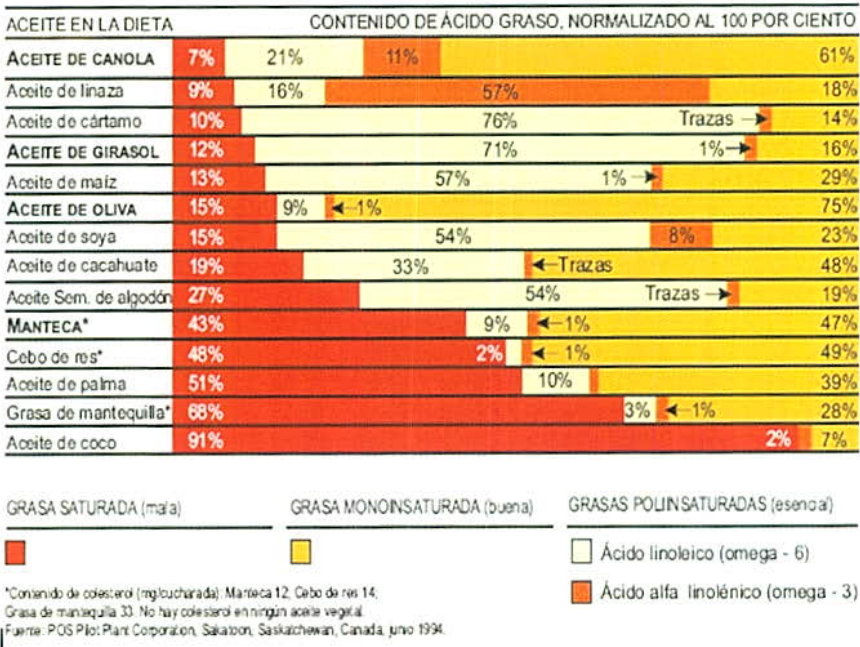
sido analizada para una alta variedad de productos y se ha establecido que su aplicación está en la producción grasas sólidas¹³, entre las que se encuentran los productos de panificación.

De otra parte, el proceso industrial de hidrogenación en fase líquida de grasas y aceites fue patentado en 1902 por W. Normann después que P. Sabatier demostrara que los dobles enlaces de hidrocarburos ligeros podían ser hidrogenados en fase vapor, utilizando catalizadores de níquel o metales nobles. Es así como las técnicas para obtener fracciones de palma, tripalmitina y las desarrolladas para producir aceite totalmente hidrogenado tampoco involucran metodologías novedosas^{10,13}.

En este orden de ideas, en el mercado se encuentran disponibles, fácilmente, como productos comerciales: el **aceite de palma -- alto oleico**¹⁴, obtenido del fruto de los híbridos de la variedades de palma *Elaeis guineensis* y *Elaeis Oleífera*, el **aceite de palma totalmente hidrogenado** y la **tripalmitina**^{15 16}, por lo tanto estos elementos tampoco representan ninguna innovación.

Ahora bien, adicional al conocimiento ya existente sobre el aceite de palma y sus fracciones, en el estado de la técnica también se había establecido el contenido de grasas saturadas, insaturadas y polinsaturadas, que hacen parte de la composición de los diferentes aceites utilizados en el sector de alimentos, en las figuras 1 y 2 se evidencia la proporción presente de estos, tanto en aceites líquidos como aceites sólidos.

Figura 1. Comparación de grasas en la dieta



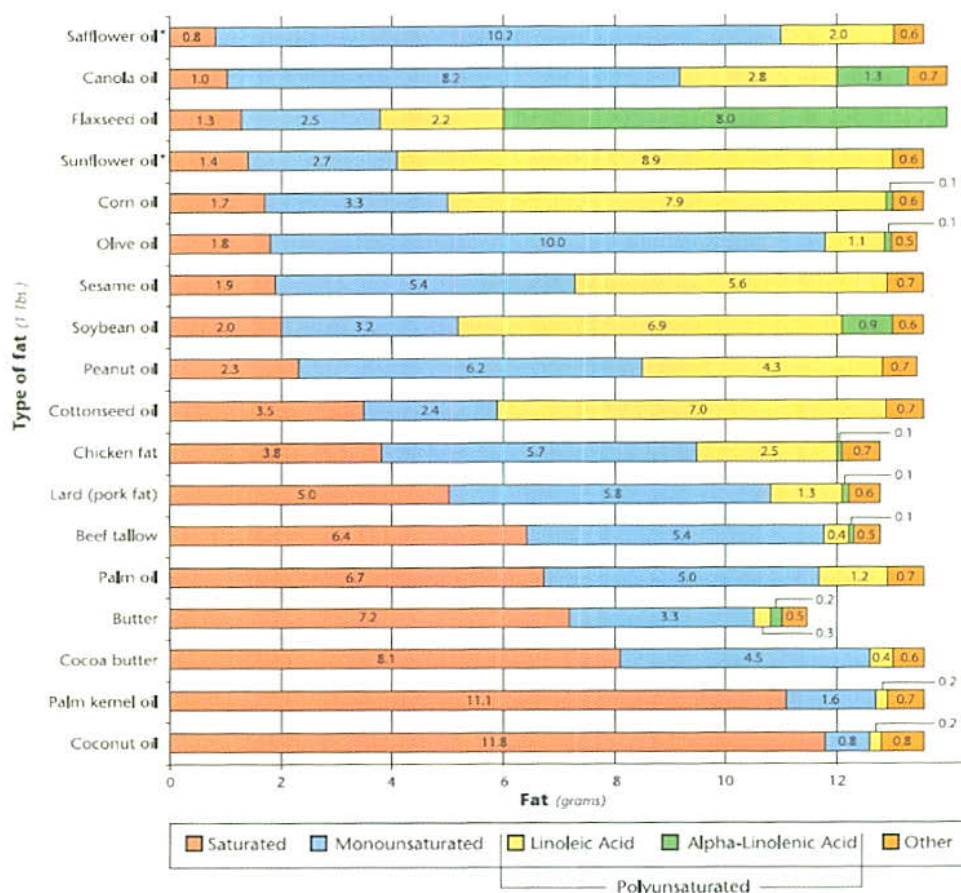
¹⁴ www.acepalma.com/Productos.php#Aceites05

¹⁵ Hoja técnica de Seguridad del Material TRIPALMITIN. Producto de MP Biomedicals, LLC. www.mpbio.com

¹⁶ 2010- Correa R., Badan A., Masuchi M., Gioielli L., Guaraldo L., Oliveira A., Pavie L., Grimaldi R. "Tripalmitin and monoacylglycerols as modifiers in the crystallisation of palm oil". Food Chemistry 122 (2010) 1185-1192



Figura 2. Comparación del contenido de ácidos saturados, monosaturados y polisaturados en diferentes aceites comestibles.



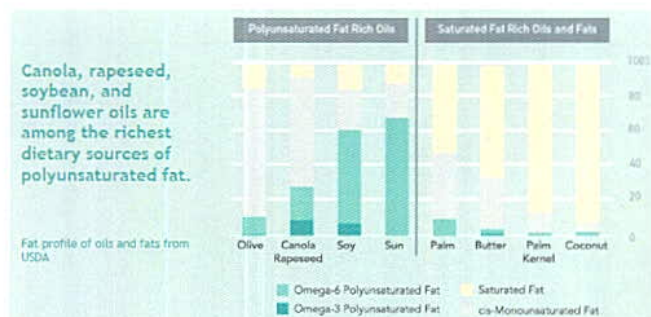
* Safflower and sunflower oils can be high in polys or monos. Most safflower oil sold in bottles is the high-oleic (high-mono) variety shown here, but some brands that are sold in health food stores are the high-linoleic (high-poly) variety. The sunflower oil sold in bottles is usually high in polys (as shown here), but most chips and other

packaged foods that are made with sunflower oil use the high-mono variety.

Sources: USDA Nutrient Database for Standard Reference (Release 14), the National Sunflower Association, and the Flax Council of Canada.

Como una persona versada en la materia sabe, a partir de los datos disponibles sobre la composición de estos aceites, se pueden realizar infinitas mezclas. Así por ejemplo, si se desea obtener una grasa sólida con bajo contenido de saturados, se podrán combinar aceites líquidos, muy bajos en saturados, con grasas o aceites sólidos (tal como el aceite de palma o sus fracciones de más alto punto de fusión). La proporción de saturados/insaturados se puede establecer fácilmente partiendo la combinación del contenido de ellos en los diferentes aceites comestibles y la cantidad en que ellos serán incorporados en la mezcla dependerá del tipo de producto a elaborar y de las características propias de dicho producto.

Sumado a lo anterior, también se sabía que existían a nivel mundial varios aceites ricos en ácidos grasos insaturados, como son el aceite de cártamo alto en oleico (safflower oil*), canola (nombre genérico para el aceite de colza bajo en ácido erúico), girasol: estándar, alto y medio oleico, aceite de maíz, de algodón, de soja, de sésamo o ajonjolí, los cuales son líquidos a temperatura ambiente y que para producir grasas sólidas a partir de ellos, tradicionalmente se pueden utilizar técnicas de hidrogenación parcial, en desuso por su relación con la producción de isómeros trans, o por hidrogenación total o la más común que es hacer mezclas con aceites saturados.



Fuente: <http://www.bunge.com/nutrition/oilseeds.html>

Completando la idea anterior, es importante señalar que la composición de los aceites comestibles determinada por métodos establecidos muestra que al realizar una mezcla física entre aceites de diferente composición (saturado e insaturado), el producto resultante tendrá una composición relativa ponderada de ácidos grasos saturados e insaturados según se requiera.

Basados en estos conocimientos, desde hace años, se encuentran en el mercado varios productos elaborados a partir de mezclas^{17 18 19} como las propuestas en la patente objeto de discusión, y algunos ejemplos de dichos productos son citados en documentos anteriores a la fecha de la patente, como se observa en las referencias indicadas^{3 4 5 6 7}, que estudian o referencian mezclas de un aceite saturado (aceite de palma y/o sus fracciones) con un aceite insaturado, para elaborar diferentes productos sólidos libres de trans y se deduce que los productos finales tendrán un contenido menor de ácidos grasos saturados.

En vista de la información anterior, es evidente que cualquier persona versada en la materia que cuente con la información suministrada en las figuras 1 y 2 está en capacidad de producir grasas bajas en saturados a partir de mezclas de aceites, manteniendo el concepto simple de combinar un aceite saturado, o sus fracciones, con un aceite insaturado. Dadas las características del aceite de palma y el amplio conocimiento que existe sobre él y sus componentes, muy seguramente cualquier técnico de este campo emplearía dicho aceite, o sus fracciones, como componente sólido y esperaría que la grasa resultante tuviera las características de apariencia, estabilidad y plasticidad determinadas por el contenido de sólidos aportado por la parte saturada.

1.2 Nivel inventivo de la invención reivindicada.

Según el Artículo 14 de la Decisión 486 de la Comisión Andina “*Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial.*”.

¹⁷ 2006 – Tarrago-Trani MT, Philips K, Lemar LE, Holden JM. “**New and Existing Oils and Fats Used in Products with Reduced Trans-Fatty Acid Content**”. Journal of the American Dietetic Association. June 2006, Volumen 106, Number 6. pp 867-880

¹⁸ 2006 – Nurhan Dunford. “*Formulación de Productos Bajos en Grasas Trans*” Mundo Alimentario. Enero/Febrero 2006 pp 16-18

¹⁹ 2011 – Baking & Snack. April 2011 – pp 57-58



De acuerdo con el Artículo 18 de la misma Decisión “*Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica.*”

Como se demuestra a continuación, la solicitud de patente de la referencia no cumple con el requisito de tener nivel inventivo:

De acuerdo con la descripción de la solicitud de **TEAM FOODS COLOMBIA S.A.**, el problema a resolver era obtener un producto con bajo contenido de ácidos grasos saturados, libre de trans-isómeros, y que fuera útil para la industria de alimentos, de modo que pudiera ser utilizado como ingrediente para la elaboración de productos de panificación y para freído industrial.

La propuesta planteada en la solicitud bajo estudio es un producto graso caracterizado porque comprende tres elementos:

1. *Aceite de palma,*
2. *Aceite líquido, y*
3. *Una base grasa constituida por una fracción enriquecida con tripalmitina y/o tripalmitina pura y/o aceite de palma completamente hidrogenado,*
Donde la fracción enriquecida con tripalmitina contiene al menos 20% de tripalmitina, el porcentaje de (1) aceite de palma es de 40% a 60% y el porcentaje (2) aceite líquido es de 20% a 60%. (El subrayado es nuestro)

El estado de la técnica más cercano es la solicitud WO 96/39855 de Unilever, que reporta la composición de un producto graso, específicamente una margarina o esparcible, que según la información de la página 11, líneas 15 a 28 comprende aceite de palma, aceite líquido y una base grasa compuesta de aceite de palma hidrogenado.

La comparación de la información divulgada en WO 96/39855, citado como documento D1 por esa Superintendencia, y la invención ahora reivindicada por **TEAM FOODS COLOMBIA S.A.**, permite establecer que las diferencias existentes entre la composición reivindicada en la solicitud de la referencia y la definida en WO 96/39855 son la proporción en que el aceite de palma está presente en la mezcla y el hecho que el producto graso que en ella se describe es un producto esparcible, o sea una margarina, que es la mezcla homogenizada de un producto graso y el agua.. Dentro de este contexto, mientras la solicitud bajo análisis establece que dicho aceite está en una proporción de 40% a 60%, la composición de Unilever no supera el 20% o 23%.

Como se muestra a continuación, a pesar de existir las diferencias antes mencionada y por ende, la mezcla reclamada cumplir con el requisito de novedad, no existe ningún efecto inesperado o sorpresivo relacionado con la proporción de aceite de palma presente en la mezcla.

En primer lugar y como se expresó a lo largo del numeral 1.1 de este documento, la necesidad de obtener un producto con bajo contenido de ácidos grasos saturados, libre de trans-isómeros, y que fuera útil para la industria de alimentos, específicamente como ingrediente para la elaboración de productos de panificación y para freído industrial ya había sido reportada. Incluso, el documento “*Decreasing Trans and Saturated Fatty Acid*



Content in Food Oils"² indica: "la industria de aceites comestibles tiene varios procesos y estrategias de reformulación capaces de reducir el contenido de trans y ácidos grasos saturados de los aceites alimenticios y aumentar su valor saludable".

Complementado esta idea, el citado artículo va más allá y afirma que: "El triángulo de calidad de los aceites comestibles ha sido descrito como aquel que tiene estabilidad oxidativa, funcionalidad y nutrición como los tres soportes. La grasa o aceite ideal debería tener excelente estabilidad oxidativa a altas temperaturas y a temperatura ambiente, contener suficiente grasa sólida para ser usada en margarinas, panadería y freído industrial, y ser tanto bajo en grasas saturadas como alto en ácidos insaturados para satisfacer los requerimientos del triángulo." Como el examinador podrá notar, el producto graso reivindicado sigue los parámetros establecidos en dicho artículo y busca reducir grasas saturadas aumentando la cantidad de ácidos insaturados.

De acuerdo con lo establecido en dicho documento, el aceite de palma, que por naturaleza no contiene ácidos trans y posee aproximadamente el 50% de ácidos saturados, resulta atractivo para ser usado en la elaboración de productos grasos sólidos, en particular, cuando se han realizado modificaciones por interesterificación y/o ha realizado fraccionamiento. Este último proceso ha permitido la obtención de muchas fracciones a partir del aceite de palma, estas fracciones han sido incorporadas en la elaboración de grasas, incluidas mantecas para panadería. Sin embargo, en la búsqueda de bajar o eliminar los isómeros trans, una de las posibilidades ha sido el uso de fracciones del aceite de palma, ante todo en países tropicales como Colombia que es el 5º productor mundial de palma de aceite, y éste por su composición de altos saturados lleva al incremento del contenido de ácidos saturados en el producto.

La solución obvia al exceso de ácidos saturados que resultan del empleo del aceite de palma y sus fracciones es incluir en la mezcla una mayor cantidad de ácidos grasos insaturados, los cuales están presentes principalmente en los aceites vegetales líquidos, como se menciona en el artículo la tabla 7 del artículo "*Trans-Free Fats with the Products of the Oil Palm – A Selective Review*"⁷, ya eran conocidas las fórmulas de grasas o fase grasa de margarinas para panadería y demás usos de estas, que comprenden 60% de estearina de palma y 40% de aceite de colza bajo en ácido erúico (aceite de canola).

Considerando la información anterior, es obvio que para generar productos grasos bajos en saturados y en trans isómeros y útiles para panadería, como plantea el solicitante, se pueden seguir las enseñanzas de la literatura, donde se indica que un mecanismo para reducir el contenido de ácidos grasos trans y saturados en aceites o grasas alimenticias es incorporar a la mezcla fracciones de aceite de palma, que es un aceite sólido, saturado y libre de trans y en pro de reducir el contenido de saturados en la formulación se agregue un aceite insaturado, tal como los aceites líquidos seleccionados del grupo que consiste de aceite de colza bajo en ácido graso erúico, aceite de cártamo alto en oleico, aceite de girasol alto en oleico o una combinación de los anteriores.

En este orden de ideas, dado que no es nuevo mezclar aceite de palma y/o sus fracciones con aceites líquidos, la esencia de la invención estaría en la inclusión del tercer componente de la composición reclamada, es decir, la base grasa constituida por:

- una fracción enriquecida con tripalmitina y/o
- tripalmitina pura y/o



- aceite de palma completamente hidrogenado.

Teniendo en cuenta que el conector de las tres opciones de base grasa están unidas mediante la conjunción “o”, es evidente que mediante la reivindicación 1 realmente se protegen tres mezclas diferentes que se especifican a continuación, y por ende, es acertado citar un documento diferente para desvirtuar el nivel inventivo de cada una de dichas mezclas:

1. 40% a 60% de aceite de palma, 20% a 60% de aceite líquido, y una base grasa constituida por una fracción enriquecida con tripalmitina, donde la fracción enriquecida con tripalmitina contiene al menos 20% de tripalmitina,
2. 40% a 60% de aceite de palma, 20% a 60% de aceite líquido, y una base grasa constituida por tripalmitina pura, y
3. 40% a 60% de aceite de palma, 20% a 60% de aceite líquido, y una base grasa constituida por aceite de palma completamente hidrogenado.

Considerando la información anterior es claro que al buscar que el producto sea útil como ingrediente de panificación, es lógico que se requiera la inclusión de componentes saturados con un alto punto de fusión para que sean sólidos, que en la solicitud de patente de **TEAM FOODS COLOMBIA S.A.**, son llamadas “base grasa”, y que dicho componente sólido sea uno ampliamente utilizado para la fabricación de productos de panificación o para freído industrial, como el aceite de palma y sus derivados. A continuación se analiza cada una de estas mezclas y se establece porque ellas carecen de nivel inventivo:

- 1.2.1 Mezcla que comprende: 40% a 60% de aceite de palma, 20% a 60% de aceite líquido, y una base grasa constituida **por una fracción enriquecida con tripalmitina, donde la fracción enriquecida con tripalmitina contiene al menos 20% de tripalmitina.**

Considerando la información general de una persona versada en la material antes del 2008 y el contenido del artículo *Trans-Free Fats with the Products of the Oil Palm – A Selective Review*⁷ es claro que no existe ninguna novedad en mezclar aceite de palma y un aceite líquido, entre ellos aceite de colza bajo en ácido graso erúico, para fabricar un ingrediente graso que sirva para la elaboración de productos de panificación.

Sumado a lo dicho, es obvio incluir en la mezcla un aceite de palma o una fracción con alto punto de fusión como la estearina, que contiene una fracción rica en tripalmitina, no solo porque se sabe que ella se emplea para producir grasas sólidas óptimas para panificación, sino porque el artículo: *“Fraccionamiento en seco de los aceites de palma y palmiste y usos de las fracciones”*¹³ establece que el fraccionamiento de la estearina permite separar una estearina dura rica en tripalmitina la cual se puede utilizar para reemplazar aceites hidrogenados en mantecas y margarinas como las que se requieren para la elaboración de pasta de hojaldre (puffpastry).

En vista de la información citada anteriormente, es obvio que para elaborar un producto libre de isómeros trans se deben utilizar componentes libres de trans, como es el caso del aceite de palma, sus fracciones y los aceites vegetales líquidos no hidrogenados.



Así mismo, siguiendo las enseñanzas del estado de la técnica, si el objetivo es producir una grasa para uso como ingrediente de panadería o para freír industrialmente, es necesario que la mezcla comprenda una cantidad de aceites sólidos suficiente para que aporten la dureza y plasticidad propia de esta clase de productos. Los documentos presentados con este memorial muestran claramente que la mezcla por excelencia es aquella que reúne aceites vegetales líquidos con aceite de palma o sus fracciones. Siendo que era conocido que el aceite de palma puede ser tratado para generar una fracción oleína (líquida) y una fracción de estearina (sólida), es obvio que para desarrollar un producto graso sólido se incluya en la mezcla una fracción enriquecida con tripalmitina, como es la estearina que aún sin ser fraccionada tiene entre el 12% al 56% de tripalmitina⁴, y que incluso se agregue a dicha fracción más tripalmitina en pro de aumentar el punto de fusión, mejorar la cristalización e incrementar la estabilidad de las grasas, para así darle mayor textura al producto final.

Complementando lo expuesto en el párrafo anterior, cualquier persona versada en la materia esperaría que la estearina pura y la estearina enriquecida con tripalmitina tengan un mayor contenido de sólidos y por ende, se requiera una menor cantidad de ella para lograr la estabilidad oxidativa de la mezcla. En consecuencia, al reducir la cantidad de base grasa requerida para lograr un producto sólido se reduce el contenido de ácidos saturados y es posible incluir en el producto final una mayor cantidad de aceites líquidos, con lo que se aumentan los ácidos grasos insaturados, sin que se pierda la solidez y plasticidad del producto.

1.2.2 Mezcla que comprende: 40% a 60% de aceite de palma, 20% a 60% de aceite líquido, y una base grasa constituida por tripalmitina pura.

Como se discutió en el numeral anterior, los productos para panificación que comprenden mezclas de aceite de palma y aceite líquidos son absolutamente conocidos, y la característica novedosa de la segunda mezcla reclamada en la reivindicación 1 es el componente de la base grasa, que para este caso es tripalmitina pura.

De acuerdo a lo establecido en el artículo "*Crystallization Kinetics of Palm Stearin in Blends with Sesame Oil*"⁴ ya se habían realizado mezclas de aceite líquido con tripalmitina pura y se sabía que la tripalmitina es el componente que mayor temperatura de fusión tiene en el aceite de palma, por lo que se espera que aumente la temperatura de fusión de la mezcla. Además, se había sido establecido que la tripalmitina afecta la cinética de cristalización y el comportamiento polimórfico del aceite de palma y la estearina. Según este artículo, la tripalmitina favorece su cristalización y promueve la cristalización de otros triglicéridos de bajo punto de fusión (cristalización heterogénea). Siendo así, resulta lógico incluir en una mezcla de aceite de palma y aceite líquido una cantidad de tripalmitina pura, la cual no solo sube la temperatura de fusión y aporta grasas sólidas a la mezcla sino que promueve la cristalización de las otras grasas presentes en ella. Dado que el producto que se desea producir es un ingrediente para panadería, es obvio que se busque que éste sea sólido y para ello la tripalmitina con su alta temperatura de fusión, su alto contenido de sólidos y su característica de estimular la cristalización heterogénea, resulta la más indicada.

Nuevamente, las propiedades de un producto graso están directamente relacionadas con los aceites que se incluyen en la mezcla que lo componen. Para el caso que nos ocupa el alto contenido de aceites sólidos y la elevada temperatura de fusión de la tripalmitina permite reducir la cantidad de aceite de palma, que es el otro componente que aporta sólidos y



saturados al producto, y aumentar la cantidad de aceites líquidos que hacen que el producto sea más suave y contenga una mayor cantidad de ácidos insaturados.

Una vez más se afirma que la invención reclamada se limita al conocimiento de la composición de los aceites comestibles y a su combinación de acuerdo con las características del producto que se desea elaborar, en este caso que el producto es una manteca o grasa para panificación o para freído industrial, libre de trans y baja en saturados es obvio que se utilicen componentes sólidos que ya han sido empleados para la fabricación de este tipo de productos, como el aceite de palma o sus fracciones o subfracciones, entre las que se encuentra la tripalmitina, y que para reducir la cantidad de saturados se incluya en la mezcla una mayor cantidad de aceites líquidos que aporten ácidos insaturados.

- 1.2.3 Mezcla que comprende: 40% a 60% de aceite de palma, 20% a 60% de aceite líquido, y una base grasa constituida por aceite de palma completamente hidrogenado.

Ahora bien, si una persona versada en la materia quiere producir una grasa sólida, sin duda alguna estaría motivada a emplear como base grasa aceite de palma completamente hidrogenado, cuya cantidad de saturados y temperatura de fusión es mayor que la reportada para el aceite de palma en estado natural. Esto último porque el documento “*Modificación de aceites y grasas en la industria de alimentos*”¹⁰ había precisado que la completa hidrogenación de un aceite vegetal líquido permite obtener grasas con mayor estabilidad a la oxidación, con un alto punto de fusión y con cero ácidos grasos trans. Además, dicho documento había divulgado que mezclas con aceite de palma completamente hidrogenado se usan para fabricar productos de panificación y chocolatería.

- 1.2.4 Argumentos que desvirtúan las afirmaciones del solicitante en relación con el nivel inventivo de la solicitud bajo análisis.

De acuerdo con los argumentos del solicitante presentados el 14 de junio de 2013 en respuesta al primer requerimiento de fondo, la pasta grasa divulgada en el documento WO 96/39855, citado como documento D1 por esa Superintendencia, se diferencia del producto reivindicado en los siguientes puntos:

- 1.2.4.1 La pasta grasa de D1 incluye hasta un 3,5% de triglicéridos POP simétricos, característica que de ninguna manera hace parte del producto graso revelado en la presente invención, el cual de ninguna manera se requiere que existe un nivel tan bajo de triglicéridos POP.

El POP es un triacilglicerol conformado por Palmítico–Oléico–Palmítico (POP) y es en parte el responsable de la naturaleza sólida del aceite de palma¹³. Dado que el documento D1 se refiere a una margarina, es obvio que se desea que ella sea fácilmente esparcible y por ende se busca que el contenido de POP sea bajo. Contrario a ello, en productos grasos para panificación, como el que se reclama en la solicitud de la referencia, se busca que el contenido de POP sea alto para asegurar que el producto graso sea lo suficientemente sólido para que pueda ser empleado como ingrediente en la elaboración de grasas de panificación.

Siendo así, para cualquier persona versada en la materia es obvio que para elaborar una grasa sólida destinada a la industria de la panificación la mezcla debe contener una mayor cantidad de POP.



1.2.4.2 La pasta grasa de D1 incluye aceite de palma hidrogenado parcialmente, toda vez que muestra un punto de fusión entre 42°C y 44°C. Contrario a esto el aceite de palma que hace parte del producto graso de la presente invención está completamente hidrogenado, mostrando un punto de fusión de 58°C y siendo esta la razón por la cual el producto es libre de ácidos grasos trans (contrario a esto, la pasta grasa de D1 comprende ácidos grasos con insaturaciones trans)

Una vez más, los componentes de la mezcla van a depender del producto que se desea obtener. Dado que el documento: *“Modificación de aceites y grasas en la industria de alimentos”*¹⁰ había precisado que la hidrogenación completa de una aceite vegetal líquido permite obtener grasas con mayor estabilidad a la oxidación, con un alto punto de fusión y libre de ácidos grasos trans y que el aceite de palma completamente hidrogenado se puede usar para fabricar productos de panificación y chocolatería, es obvio emplear aceite de palma completamente hidrogenado, pues cualquier persona versada en la materia sabe que los aceites parcialmente hidrogenados aumentan el contenido de trans en la mezcla, lo cual es absolutamente contrario al efecto que se desea obtener con el desarrollo propuesto en la solicitud de patente bajo análisis.

Adicionalmente, desde los años ochenta se sabe que los aceites vegetales parcialmente hidrogenados generan isómeros trans y siempre está tratando de reducir o eliminar la presencia de dichos los productos grasos. Siendo así, es obvio que una persona versada en la materia enfrentada al problema de reducir la presencia de trans opte en primer lugar por eliminar la inclusión de cualquier aceite parcialmente hidrogenado a la mezcla.

De igual manera, una persona versada en la materia que tuviera que diseñar una mezcla para generar un producto graso sólido apto como ingrediente para la panificación, la galletería, el freído, etc. y que sea libre de grasas trans, que hubiera tenido acceso a la información del artículo *“Modificación de aceites y grasas en la industria de alimentos”*, estaría motivada a buscar el aumento de las grasas sólidas en la mezcla mediante la incorporación de aceite de palma, o sus fracciones, completamente hidrogenado no solo porque dicho ácido tiene un punto de fusión más alto sino porque el citado documento enseña que: *“El proceso de hidrogenación total no produce ácidos grasos trans y efectivamente, se usa para fabricar productos de panificación y chocolatería”*.

En este orden de ideas, la eliminación de cualquier aceite o de aceite de palma parcialmente hidrogenado es obvia si se busca reducir la presencia de isómeros trans y la inclusión de aceite de cualquier aceite o de aceite de palma completamente hidrogenado es obvia si se desea usar como base grasa para la elaboración de un producto graso utilizado para panificación, galletería, freído, etc.

1.2.4.3 Finalmente, el solicitante señala que la pasta grasa de D1 es una base grasa para esparcibles y margarina, mientras que el producto graso revelado en la solicitud de patente en cuestión es empleado directamente en la elaboración de productos de panificación, así como en el freído de diversos productos (pasabocas, tubérculos, carnes, entre otros).

Las margarinas son productos grasos que se elaboran mezclando y emulsificando una fase grasa con una fase acuosa. La fase grasa se elabora, generalmente combinando **grasas sólidas** con un aceite. Las grasas solidas pueden prepararse con aceites hidrogenados (total



o parcialmente) y una mezcla de grasas sólidas naturales²⁰ que pueden estar, o no, interesterificadas. Como se puede observar en la definición de margarina, el producto que se pretende patentar coincide con la fase grasa que hace parte de las margarinas. Es decir que un **“producto graso sólido con bajo contenido de grasa saturada y libre de ácidos grasos trans”** mezclado y emulsionado con agua sería una margarina. Por lo cual el concepto aplica tanto para fabricar grasas para panificación como margarinas.

2. Conclusión y Petición:

La mezcla reivindicada en la solicitud en cuestión se basa en un concepto simple y ampliamente conocido por cualquier persona versada en la materia, incluso antes de la fecha de presentación de la solicitud, el cual consiste en mezclar un aceite saturado o sus fracciones para obtener una composición sólida y añadir aceites insaturados para reducir la cantidad total de ácidos grasos saturados.

Con base en lo explicado anteriormente y sustentado con la literatura referenciada desde la década de los 80, se puede concluir que el “producto graso sólido con bajo contenido de grasa saturada y libre de ácidos grasos trans”, que se pretende patentar, NO reúne los requisitos para obtener el privilegio de patente pues como se ha demostrado carece de nivel inventivo.

En tal sentido, solicitamos a este despacho hacer el uso que considere conveniente de la información suministrada, a fin de evitar que sea otorgado el privilegio de patente a un desarrollo que como demostramos no tiene nivel inventivo y que por ende, no cumple con los requisitos de patentabilidad establecidos en el artículo 14 de la Decisión 486 de la Comunidad Andina.

3. Anexos:

Me permito anexar los siguientes documentos, los cuales han sido señalados en el presente documento:

1. 2008 – Cenipalma. “Los ácidos grasos trans y la salud”. Lípidos y Salud. Volumen 9. No.4 de 2008
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4. 2000 – Toro-Vazquez JF, Briceño-Montelongo M, Dibildox-Alvarado E, Charó-Alonso M, Reyes-Hernández J. “Crystallization Kinetics of Palm Stearin in Blends with Sesame Oil”. JAOCS. Vol. 77, No. 3 pp. 297-
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6. 2006 – Noor Lida HAbi Mat Dian, Kalyana Sundram, Nor Aini Idris. “DSC Study on the Melting Properties of Palm Oil, Sunflower Oil, and Palm Kernel Olein

²⁰2005 – Griguol V., Leon- Camacho M., Vicarios I. “**Contenidos en ácidos Grasos Trans de las Margarinas: Evolución en las Últimas Décadas y Tendencias Actuales**” Archivos Latinoamericanos de Nutrición. ALAN V. 55 no. 4 Caracas Dic 2005



- Blends Before and After Chemical Interesterification". JAOCS Vo. 83, No. 8 pp. 739-
7. 2007 – Berger K.G. "Trans-Free Fats with the Products of the Oil Palm – A Selective Review". Czech J. Food Sci. , 25: pp 174-181
 8. 2008 – García D., Sandoval J., Saldaña R., Cárdenas G., Soplín J. Sotero V., Pavan R., Mancini J. "Fraccionamiento e interesterificación del aceite de palma (*Elaeis guineensis*) cultivado en la Amazonía peruana". Grasas y Aceites 59 (2), Abril – Junio 104-109. 2008
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 10. 2008 – Cenipalma. "Modificación de aceites y grasas en la industria de alimentos". Lípidos y Salud. Volumen 9. No. 1 de 2008
 11. 1989 – Yap, PH, de Man, JM, de Man ,L. "Polymorphism of palm oil and palm oil products"" Journal of the American Oil Chemists' Society. 66(5) , pp 693-697
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 13. 2004 – Cadena, AE. "Fraccionamiento en seco de los aceites de palma y palmiste y usos de las fracciones". PALMAS Vol. 225 No. Especial, Tomo II, 2004. Pp 482-491
 14. www.acepalma.com/Productos.php#Aceites05
 15. Hoja técnica de Seguridad del Material TRIPALMITIN. Producto de MP Biomedicals, LLC. www.mpbio.com
 16. 2010- Correa R., Badan A., Masuchi M., Gioielli L., Guaraldo L., Oliveira A., Pavie L., Grimaldi R. "Tripalmitin and monoacylglycerols as modifiers in the crystallisation of palm oil". Food Chemistry 122 (2010) 1185-1192
 17. 2006 – Tarrago-Trani MT, Philips K, Lemar LE, Holden JM. "New and Existing Oils and Fats Used in Products with Reduced Trans-Fatty Acid Content". Journal of the American Dietetic Association. June 2006, Volumen 106, Number 6. pp 867-880
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Los ácidos grasos *trans* y la salud*

Diversos estudios epidemiológicos desde los años ochentas han relacionado el consumo de grasas y la presencia de diversos problemas de salud, entre los cuales se pueden resaltar la enfermedad cardiovascular y el cáncer. Teniendo en cuenta estos reportes, la comunidad científica ha centrado su investigación en explicar el papel que cumplen las diferentes grasas en el metabolismo del cuerpo humano y, específicamente, en diferenciar el efecto que el consumo de cada una de ellas puede causar sobre el estado de salud o enfermedad del ser humano.

Las grasas de la dieta son ésteres de glicerol y tres diferentes ácidos grasos. Éstos son cadenas largas de carbonos, generalmente entre 16 y 20, terminadas por un grupo carboxilo. Los ácidos grasos pueden ser saturados, es decir, cada uno de sus carbonos está sustituido por dos hidrógenos o insaturados, que tienen uno o más dobles enlaces. El eje de los saturados se puede considerar para propósitos prácticos como lineal. Los insaturados de fuentes naturales son siempre *cis*, es decir, que las cadenas de carbono a lado y lado del plano del doble enlace se encuentran en la misma dirección espacial, lo que hace que el eje de la cadena se doble alrededor de 130° en relación con cada carbono del enlace.

Las propiedades físicas de las grasas dependen precisamente de estas propiedades. En efecto, a temperatura ambiente, los ácidos grasos saturados podrán acomodarse estrechamente uno al lado del otro, lo que hará que su estado físico sea sólido. Por el contrario, el doblamiento del eje de los ácidos grasos insaturados impide que se puedan acomodar estrechamente uno al lado del otro y la dificultad se incrementa con el número de dobles enlaces. Esto hace que a temperatura ambiente estos ácidos grasos sean líquidos. Puesto de otra manera, el punto de fusión de los ácidos grasos es una gama que va desde muy bajo para los poliinsaturados, hasta alto para los saturados, dependiendo del número de dobles enlaces presentes.



Aceite de palma y sus fracciones: opciones cero *trans* para formulación de alimentos.

A esta propiedad se le debe añadir otra: el punto de fusión se incrementa con el largo de la cadena, por lo que ácidos grasos saturados de 20 carbonos serán sólidos a temperaturas más altas que aquellas de 16 carbonos. Teniendo en cuenta que la grasa natural está compuesta generalmente por tres diferentes tipos de ácidos grasos, sus propiedades físicas dependerán de la proporción en la que estos se encuentren en el triglicérido. Los ácidos grasos más comunes en la grasa de la dieta son saturados de 16 y 18 carbonos e insaturados de 18 a 24 carbonos, y su composición exacta depende de la fuente natural de la grasa.

El aceite de palma se obtiene de la palma *Elaeis guineensis*. En el mundo es el segundo aceite comercial más utilizado (29%) después del de soya (30%), pero el uso depende del país, ya que, por ejemplo, en Estados Unidos constituye apenas el 2% del total¹. Colombia es el quinto país productor de aceite de palma, y se utiliza generalmente para hacer mezclas comerciales con otros aceites que se obtienen bajo diferentes nombres en los supermercados. El

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aceite de palma colombiano, en promedio, está compuesto de 43% de ácidos grasos saturados² y 54 % de ácidos grasos insaturados. El aceite de palma consumido en Costa Rica³ tiene una composición similar, con 48% de ácidos grasos saturados y 52% de insaturados, de los cuales el 38% es oléico y el 11% es linoléico. Se ha reportado que la composición del aceite asiático es 51% y 49%. La composición palmítico: oléico: linoléico de la palmoleína colombiana, es 30:33:15, que también es diferente a la asiática cuya composición es 45:39:11.

Metabolismo de ácidos grasos

Las células del organismo humano sintetizan ácidos grasos a partir de la acetil CoA, metabolito que se encuentra en una encrucijada metabólica, ya que es el producto final de la degradación inicial de los monómeros de carbohidratos, grasas y aminoácidos y, a su vez, es la sustancia que, de acuerdo con la economía temporal de la célula, puede entrar al ciclo de Krebs para su degradación final a CO₂ y H₂O y producción de energía, o puede ir a formar ácidos grasos cuando hay exceso de ingesta; en el caso del hígado en ayunas, puede ir a formar glucosa a través de la gluconeogénesis.

Cuando la ingesta supera las necesidades energéticas del organismo, la acetil CoA es convertida, a través de un proceso metabólico estrictamente controlado y que requiere energía y equivalentes reducidos, a palmitoil CoA y, a partir de ella, a estearil CoA y a Oleil CoA. La poca disponibilidad de CoA permite su reciclaje a través de la utilización de las acil CoA's como sustrato para unirse a glicerol y formar triglicéridos (TG) que tienen la ventaja de ocupar muy poco espacio celular ya que, siendo hidrofóbicos, se unen para formar gotitas de depósito que en algunas células, tales como los adipocitos, pueden llegar a ocupar la mayor parte del citoplasma.

Nótese que en el proceso sólo se forma un ácido graso insaturado, el oléico, cuyo doble enlace es *cis*, lo que implica un cambio en el eje de la cadena hidrocarbonada que impide su empaquetamiento y le da las propiedades de fluidez necesarias a temperatura corporal. Este mismo proceso se da en vegetales, particularmente en aquellos cuyas semillas contienen una gran cantidad de aceite. En este caso, no sólo se produce el ácido oléico monoinsaturado, sino que se biosintetizan diversos ácidos grasos con un número mayor no sólo de carbonos sino de dobles enlaces, todos ellos de tipo *cis*, dándoles a los aceites esa característica de ser líquidos a temperatura ambiente. En el caso de ciertos peces, particularmente los salmónidos, encontramos también la biosíntesis de ácidos grasos poliinsaturados de has-

ta 22 carbonos y hasta seis dobles enlaces, todos ellos de tipo *cis*.

A pesar de que el organismo humano sólo puede sintetizar palmitato, oleato y, en mucha menor cantidad, otros ácidos grasos tales como el palmitoleico y el esterárico, la grasa de los tejidos está compuesta no sólo de los ácidos grasos propios, sino de los provenientes de la dieta. Estos últimos se distribuyen a los tejidos a través de los quilomicrones sintetizados en los enterocitos, las lipoproteínas de muy baja densidad (VLDL) sintetizadas en el hígado y su producto de degradación parcial, las lipoproteínas de baja densidad (LDL).

Síntesis de lipoproteínas

La síntesis de lipoproteínas se lleva a cabo en el retículo endoplásmico liso de las células, a través de un proceso que, en el caso de enterocitos y hepatocitos, se inicia con la síntesis de una proteína muy grande, la apoproteína B, quizás la más larga de las proteínas del ser humano. A medida que se va sintetizando la cadena, se unen a ella triglicéridos y ésteres de colesterol (ECol). Debido a sus características físicas, una mezcla adecuada de TG y ECol compuestos por ácidos grasos con más o menos dobles enlaces, definirá la cantidad total de grasa que se puede unir a la apoproteína. Así, si predominan los ácidos grasos insaturados como en el caso de los enterocitos que los reciben de la dieta, fundamentalmente los TG en este caso ocuparán mucho más espacio para la misma masa molecular y, por consiguiente, la densidad será muy baja.

En el caso del hígado que tiene a su disposición los ácidos grasos propios en los que los saturados pueden ser altos y los que llegan en los remanentes de quilomicrones que provienen de la dieta y, por consiguiente, tienen muchas más insaturaciones, el empaquetamiento va a ser un poco más estrecho y el volumen de TG y ECol para la misma masa va a ser un poco menor que en el caso de los quilomicrones y, por ende, su densidad va a ser mayor. De la anterior discusión debe quedar claro que la grasa de la dieta es de primordial importancia en la composición y densidad final de las VLDL.

En efecto, cuando la ingesta de colesterol y de ácidos grasos saturados es alta, al hígado llegarán esos ácidos grasos como TG y ECol. Los TG serán hidrolizados y habrá mayor disponibilidad de ácidos grasos saturados para la síntesis de los TG de la VLDL. Los ECol podrán ser utilizados directamente. El resultado es una VLDL más densa. Cuando las VLDL son metabolizadas en la circulación, se hidrolizan los TG que son usados por los tejidos, pero

no así los ECol. Esto hace que la densidad de la partícula se haga cada vez mayor. Una interesante observación es que las partículas de mayor densidad tienen una vida media en circulación más alta, lo que en términos fisiológicos implica que la concentración de LDL se incrementa en sangre.

Ácidos grasos *trans* y síntesis de lipoproteínas

En la naturaleza los ácidos grasos *trans* no se encuentran en cantidades significativas, ya que su única fuente es la leche de rumiantes, que contiene trazas de las producidas por sus bacterias intestinales. Sin embargo, la actividad industrial que está dirigida a satisfacer el gusto de los consumidores ha producido diferentes tipos de grasas semisólidas para mesa y para cocina, margarinas y shortenings, que pretenden sustituir las provenientes de la leche. Los procedimientos que consisten en hidrogenación parcial de los dobles enlaces, para permitir su mejor empaquetamiento a temperatura ambiente, desafortunadamente no son un proceso con un solo producto, ácidos grasos saturados, sino que tiene como subproducto ácidos grasos con enlaces *trans*.

Esta es la mayor fuente de ácidos grasos *trans* en la dieta. Mittmesser y Carr⁴ mostraron que la adición de ácidos grasos totales (AGT) *in vitro* a células de hepatoma altera tanto la secreción como el tamaño de partículas de apoB₁₀₀. En sujetos se encontró también una disminución del catabolismo de LDLapoB₁₀₀ y aumento en el catabolismo de la apoAI⁵, así como una disminución del tamaño de las LDL⁶.

Como se señaló más arriba, los ácidos grasos *trans* tienen las mismas características físicas de los ácidos grasos saturados, y su incorporación a las VLDL tendrá los mismos resultados, es decir, un incremento en las LDLc. De esta manera, tanto los ácidos grasos saturados como los *trans*, incrementan las LDLc, condición necesaria, aunque no suficiente para desarrollar enfermedad cardiovascular, particularmente cuando es concomitante con marcadores de inflamación.

Ácidos grasos *trans* y enfermedad cardiovascular

El consumo de 5 g diarios de AGT se ha relacionado con un 25% de incremento en el riesgo de sufrir un accidente cardíaco isquémico⁷. Stender y Dyerberg, del Consejo Danés de Nutrición, reportaron⁸ que el consumo de AGT, peso/peso, representa un riesgo de adquirir ECV de 2.5 a 10 veces más alto

que el consumo de ácidos grasos saturados. Señalan, además, que los AGT tienen un efecto negativo tanto en la etapa fetal como en la neonatal de los niños, se incrementa el riesgo de cáncer de colon.

Sugieren mayores estudios para determinar el posible efecto sobre las enfermedades alérgicas de los niños y en el riesgo de la diabetes del adulto. Informan que el gobierno danés prohibió la venta de aceites y grasas que contienen más del 2% de AGT, a partir de enero de 2004. Mozzafarian y col⁹ encontraron a partir de un metanálisis de 39 estudios diferentes con 524 sujetos, que el reemplazo del 1% de la energía por AGT disminuía HDLc e incrementaba la relación Colesterol Total/HDL. La magnitud del incremento variaba así: sustitución isocalórica de AGS por AGT, 0,02; AGM, 0,05 y AGPI, 0,052. De acuerdo con los autores, este cambio se podría deber a que los AGT incrementan la actividad de la proteína de transferencia de colesterol ésteres de plasma¹⁰, ya que esta enzima es la que transfiere colesterol ésteres de HDL a LDL.

Craigh-Smith publicó en 2006¹¹ un estudio del consumo de ácidos grasos en diferentes países del mundo y encontró que para 1999 el consumo diario promedio por persona en Canadá era 6.8 g, en Estados Unidos de 5.3 g, en los países europeos del norte entre 2.5 y 5 g y en los países mediterráneos, menos de 2g. En un reciente estudio¹² en el que se comparó la concentración de AGT en 170 g de papas fritas y 160 g de pollo (nuggets) en McDonald y Kentucky Fried Chicken de diferentes países, se encontró que en todos los países europeos, con excepción de España, EE.UU. y Perú, esta porción provee más de 5 g de AGT. Aunque un estudio similar no se ha hecho en Colombia, es de presumir que no se aparte mucho de lo encontrado en otros países.

A pesar de que la mayor parte de los estudios relacionan el contenido total de AGT con el riesgo de desarrollar ECV, Baylin y col¹³ encontraron una relación positiva entre la concentración de AGT 18:2 en el tejido adiposo de adultos que sufrieron un infarto no fatal en Costa Rica. Como era de esperar, la fuente de 18:2 AGT es principalmente aceite de soya parcialmente hidrogenado. Los autores llaman la atención a esta relación, ya que estudios similares que se han llevado a cabo en Seattle (EE.UU.) y en Europa lo relacionan con 18:1 AGT que proviene principalmente de productos lácteos.

Otros efectos

Mozzafarian¹⁴ ha reportado que los AGT incrementan interleukinas relacionadas con inflamación y propone que esto se podría deber a su incorporación a

fosfolípidos. Aunque actualmente se desconoce el mecanismo de esta acción, es importante recordar que los fosfolípidos tienen una importancia muy grande en los procesos de señalización celular¹⁵. A propósito de esta relación, Lemaitre y col¹⁶ encontraron que niveles altos de 18:2 AGT y niveles bajos de 18:1 AGT en fosfolípidos del plasma y en fosfolípidos de la membrana de glóbulos rojos están asociados con un riesgo más alto de muerte cardíaca súbita y mortalidad por enfermedad isquémica coronaria. Sun y col¹⁷, analizando los datos del estudio de salud de 39.000 enfermeras entre 1989 y 1990, encontraron que el contenido total de AGT en eritrocitos correlacionaba significativamente con el consumo de la AGT de la dieta y con incrementos en LDLc y disminución de HDLc. Basados en este mismo estudio, el mismo grupo encontró que el consumo de AGT también afecta la función endotelial¹⁸. Finalmente, el consumo de AGT se ha relacionado con el

riesgo de desarrollar cáncer de próstata¹⁹ y de producir cálculos biliares.²⁰

Conclusiones

Como han demostrado diversos autores, el consumo de AGT procedentes en su mayoría de la hidrogenación parcial de aceites vegetales (ácidos grasos *trans*) incrementa en forma sustancial los factores de riesgo de desarrollar enfermedad cardiovascular en mucho mayor grado que el consumo de grasa saturada, razón por la cual, es de imperativa importancia que se regule este componente como parte de los alimentos. Los mecanismos de esta acción no están claros, pero podrían deberse a las propiedades físicas de los AGT que incidirían en la síntesis de VLDL.

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Decreasing *Trans* and Saturated Fatty Acid Content in Food Oils

The edible oil industry has various processing and reformulation strategies available to decrease the *trans* and saturated fatty acid contents of food oils to increase their health value.

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On July 11, 2003, the Food and Drug Administration published final rules mandating *trans* acid content to be included on food labels by January 1, 2006, in accordance with the Nutrition Labeling Act of 2003. This ruling will have a profound effect on the food and edible oil industries. This article provides some background and describes some strategies that will permit the food industry to comply with the new regulations.

Trans Fats

Fats and oils are triglycerides containing both saturated and unsaturated fatty acids. Typically, common vegetable oils, including soybean, corn, cottonseed, sunflower, peanut, and olive, are relatively low in saturated acids, and the double bonds within unsaturated acids are in the *cis* configuration. To improve their oxidative stability and to increase their melting points, vegetable oils sometimes require hydrogenation. This is particularly true for margarines, spreads, shortenings, and frying fats. During catalytic hydrogenation, some of the double bonds are isomerized from the naturally occurring *cis* form to the *trans* form. *Trans* acids may also be formed in the rumen of animals. Butter, milk, beef tallow, and lard contain small amounts (2-5%) of *trans* acids.

The roles of saturated and *trans* acids in human health and nutrition are highly controversial issues. Nevertheless, in 1990, Congress passed the Nutrition Labeling and Education Act, and by 1994, labeling guidelines had been published. Of particular interest are statements regarding fat. Listing of "Total fat" must be in grams and in bold print. Listing of "Saturated fat" must be in grams, but is not required if the food contains less than 0.5% of total fat per serving and if no claims are made about fat and cholesterol content. If not required and not declared, the statement, "Not a significant source of saturated fat" must be included at the bottom of the nutrition label. Listing of "Polyunsaturated" in grams is voluntary, unless "Monounsaturated fat" or "Monounsaturated" is declared or a cholesterol or saturated fat claim is made and the total fat declared is greater than zero. Listing of "Cholesterol" must be in milligrams and in bold print, but is not required if the product contains less than 2 mg of cholesterol per serving and makes no claim about fat.

saturated fat, or cholesterol; and, if not declared, the statement, "Not a significant source of cholesterol" must be included at the bottom of the nutrition label.

Several groups petitioned the Food and Drug Administration to include *trans* acids as part of the nutrition label, and proposed rules issued in 1999 mandated both *trans* labeling and statements to the effect that *trans* acid consumption should be kept to a minimum. After opening the rules for public comment several times, final regulations were issued on July 11, 2003 (FDA, 2003). By January 1, 2006, *trans* content will be required as a separate line on labels, but the aforementioned statement regarding consumption was eliminated.

Soybean and Palm Oils

An edible oil quality triangle has been described as having oxidative stability, functionality, and nutrition as the three legs (Lui, 1999). The ideal fat or oil should have excellent oxidative stability at high and ambient temperatures, contain enough solid fat for use as margarines, shortenings, and frying fats, and be both low in saturated fatty acid, and high in polyunsaturated acids, thus satisfying the requirements of the triangle. However, no single fat or oil fully satisfies these requirements.

Worldwide consumption of edible fats and oils in 2001-02 amounted to just over 92 million metric tons, of which 59% can be accounted for by soybean oil (29 million metric tons) and palm oil (25.4 million metric tons). While soybean oil is relatively low in saturated acids (15%), it represents a major source of *trans* fatty acids in our food supply because it must be hydrogenated to achieve functional properties and oxidative stability for use in salads/cooking, shortenings, and margarines/spreads. On the other hand, palm oil, while containing no *trans* acids, contains about 50% saturated acids, making it attractive for use in the these products, particularly when modified by interesterification and/or fractionation.

Thus, just two fats and oils dominate and dictate oil processing worldwide, and any discussion of strategies to reduce *trans* and saturated acids in the food supply must focus on soybean and palm oils.

To improve the quality triangle for functionality and oxidative stability, various fat-modification techniques--hydrogenation, interesterification, fraction-

Just two fats and oils, dominate and dictate oil processing worldwide, and any discussion of strategies to reduce *trans* and saturated acids in the food supply must focus on soybean and palm oils.

ation, and combinations--are employed by the industry. A decade ago, it was estimated that about one-third of the edible oils produced worldwide were hydrogenated, while 10% were processed by interesterification/fractionation (Hau-mann, 1994). While more recent data are lacking, it is anticipated that the latter techniques will see increased usage in the future.

Over the past several decades, a number of oilseeds have been introduced with modified fatty acid composition. These include canola and soybean oils with low linolenic acid content; corn, soybean, and sunflower oils with high oleic acid content; and soybean oils with high saturated acids and low saturates (Lui, 1999; Gunstone, 2001; Gupta, 1998, 2001).

Many of these oils show promise in reducing *trans* and/or saturated acids in food oils because the high-oleic oils are much more oxidatively stable and do not require hydrogenation, while the high-saturated oils are *trans* free.

Improvements in oil processing technology also provide options for *trans* and saturated acid reduction. Traditional random interesterification, in which fatty acids are redistributed across the glycerol backbone, is usually accomplished with a chemical catalyst and is thus nonspecific. Numerous advances have been made by use of enzymes which are stereo-specific, allowing production of tailor-made fats (MacRae, 1983). Indeed, shortening and confectionery fats are now produced commercially by this technology. The time-honored hydrogenation process offers potential for reducing *trans* acids in food oils (Hasman, 1995; King et al., 2001; Warner et al., 2000).

Trans and Saturated Acid Contents

Nearly 18 billion lb of soybean oil are consumed domestically per year, as follows: shortening 8.57 billion lb; margarine/spreads 1.24 billion lb; salad/cooking oil 7.9 billion lb; and other edible products 125 million lb (Soyatech, 2003). The shortening and margarine categories contain hydrogenated components. Based on the assumption that soft and stick margarines/spreads contain an average of 15% *trans* acids and shortenings contain an average of 20% *trans* acids, about 1.9 billion lb of *trans* acids are produced each year by hydrogenation.

During 2000-01, corn oil consumption amounted to 1.41 billion lb, canola oil 1.75 billion lb, and cottonseed oil 767 million lb. No data are available on the amounts of these oils going into shortenings, marga-

Table 1--*Trans* and saturated acid consumption in the United States, 2001-02

Oil/fat	Consumption (billion lb)		
	Total	<i>Trans</i> acids	Saturated acids
Soybean spreads	1.24	0.186	0.38
Soybean shortening	8.57	1.714	1.97
Soybean salad/cooking oil*	7.9	0.79	1.185
Corn oil	1.345	—	0.18
Cottonseed oil	0.767	—	0.203
Canola oil	1.793	—	0.129
Coconut oil	1.1	—	1
Palm oil	0.455	—	0.205
Palm kernel oil	0.471	—	0.409
Lard	0.989 ^b	0.01	0.392
Tallow	1.47 ^c	0.07	0.401

^aMay contain *trans* acids, about 10%
^b1-2% *trans*
^c4-5% *trans*

rines, and salad cooking oils.

Significant amounts of edible food and oils high in saturated acids are consumed per year in the U.S., including coconut oil 1.1 billion lb, lard 989 million lb, palm and palm kernel oils 826 million lb, and edible tallow 1.47 billion lb—a total consumption of 2.48 billion lb of saturated acids.

Thus, the U.S. consumption of *trans* and saturated acids is about equal—1.9 vs 2.48 billion lb, respectively. The value for *trans* consumption is low because of lack of data for the amounts of corn, cottonseed, and canola oil processed by hydrogenation (Table 1).

A survey of the *trans* content of soft tub margarine/spreads in the U.S. was reported by List et al. (2000). The samples were premium products that were taken from grocery store shelves and, according to their label, were formulated from hydrogenated and liquid soybean oil. From 1992 to 1999, the overall *trans* reduction ranged from about 25% to 82%, with an average reduction of nearly 56%. The 1992 data indicate an average of nearly 20% *trans* in soft tub products, whereas the 1999 data show less than 9% *trans*. Stick/spreadable products have shown decreased *trans* acid contents over the past decade—*trans* acids averaged 26.8% in 1989, but by 1999 the average had dropped to 16.9%, a 37% overall reduction (Postmus et al., 1989; List et al., 2000).

Thus, the domestic edible oil industry has made concerted efforts to reduce *trans* acids in edible products. This has been accomplished through reformulation methods in which a multiple basestock system employing three hydrogenated oils has been replaced with a single hydrogenated component. Typically, soybean oil, hydrogenated to an iodine value (IV)—a measure of degree of unsaturation—of about 65 (40% *trans*), is blended with 25–50% liquid soybean oil to yield components suitable for a wide variety of spreads, including soft tub, spreadable stick, and stick products.

The *trans* acid content of margarines and spreads taken from the literature over a seven-year period (1995–2002) show some interesting trends in oil processing (Alonzo et al., 2000; Oveson et al., 1998; Ratnayke et al., 1998; Tsanev et al., 1998; Tekin et al., 2002; Bayard and Wolff, 1995). Low-*trans* products are arbitrarily defined as those having 5% or less *trans* acids, while zero-*trans* products may have smaller amounts (1–2%). Of the 228 samples reported, 87(38.2%) may be considered zero- or low-*trans*. The largest number of samples reported include those from Canada and the U.S., where 10 of the 126 were zero- or low-*trans*.

These results indicate that margarines/spreads formulated in North America are formulated primarily from hydrogenated components rather than by interesterification. The products produced in Denmark are formulated from interesterified oil components and represent the only country surveyed where hydrogenation has been replaced entirely. However, if the 59 samples from Denmark are excluded, 28 of 169 (16.6%) were low- or zero-*trans*. Thus, it would appear that hydrogenation remains the technology of choice to formulate margarine/spread products throughout most of the world.

Matsuzaki et al. (2002) analyzed margarines marketed in 11 countries, including Europe, Scandinavia, and the U.S., for their *trans* fatty acid and other compositional data. Their data confirm that any decrease in *trans* fatty acids is achieved at the expense of increased saturated acids content. Margarines produced in the U.S. had the lowest *trans*/saturated acid content (41.4%) and the highest ratio of polyunsaturated fat-

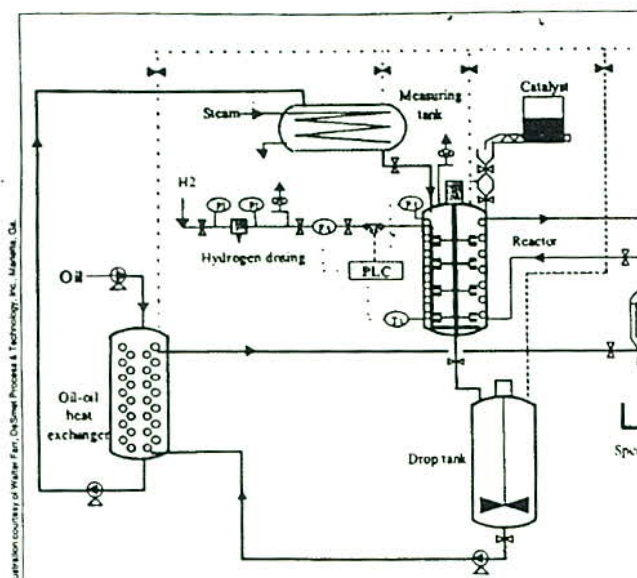


Fig. 1—Hydrogenation flow diagram. Oils are hydrogenated to increase *t* improve their melting properties by increasing their degree of saturation primary cause of formation of *trans* fatty acids.

ty acids/*trans* fatty acids plus saturated acids compared to the rest of the world. The same trend was observed for soft tub margarines.

Hydrogenation of Soy-Based Oils

Fig. 1 is a flow diagram of the hydrogenation process. Temperature, pressure, agitation, and catalyst concentration are the most important factors governing the course and speed of hydrogenation. However, with other factors being equal, temperature has the largest effect on *trans* acid formation. Industrially, hydrogenation is carried out under selective conditions favoring reduction of polyunsaturated groups over that of monoenic acids.

Typically, selective conditions involve high temperature (160–220°C) and low hydrogen pressure (10–40 psi) in the presence of 0.02–0.04% nickel metal catalyst supplied as 25% nickel on a support. Although selective conditions promote *trans* fatty acid formation, it is imperative that the amount of stearic acid formed at lower IVs be kept at a minimum, since any tristearin formed in the reaction will unduly raise the melting point of the finished oil such that the sharply melting

“*trans*” functionality is compromised.

Partially hydrogenated winterized soybean salad/cooking oil (PHWSBO) has been produced commercially in the U.S. since the early 1960s. It is typically produced by hydrogenation under selective conditions (160–170°C, low hydrogen pressure, and 0.02% nickel) where the IV is reduced from approximately 130–132 to 110–115. The feedstock is then chilled slowly, allowing the higher-melting triglycerides to crystallize. The liquid oil is then recovered by filtration. The higher-melting fraction, stearine, may be incorporated into margarine/spread or shortening products.

The composition and properties of PHWSBO are given in Table 2, along with hydrogenation

conditions used in its manufacture. The product with an IV of 110–112 will remain clear at refrigerator temperatures and is superior to unhydrogenated oil for light frying in the home.

Further discussion of the hydrogenation process can be found in reviews by Hastert (1996), Patterson (1994), and Erickson and Erickson (1995).

Margarine Basestock and Formulation of Spreads

Margarine oil basestocks—hydrogenated components that, when blended with liquid oil, produce desired functional properties—require “selective conditions” in which stearic acid formation needs to be controlled very carefully. Typically, low pressure and high temperature are used. The preparation of multi-purpose margarine basestocks involves reducing the IV of soybean oil from about 130 to 65–70 in the presence of a nickel catalyst at about 220°C and low hydrogen pressure.

Margarine oils typically show the following solid fat content (SFC): tub products 8–14 at 10°C, 4–8 at 21.1°C, and 1–

Table 2—Properties of partially hydrogenated soybean oils

Oil	Fatty acid composition					Iodine value	% <i>trans</i>	Melting point (°C)	Solid fat content				
	C16	C18	C18:1	C18:2	C18:3				10°C	21.1°C	26.7°C	33.3°C	40°C
Original soybean oil	11.2	3.7	22.1	55.0	6.8	132.0	0.0	–14.3	0.0	0.0	0.0	0.0	0.0
Hydrogenated soybean oil ^a	11.4	4.7	40.3	40.5	3.0	112.6	8.7	16.7	0.0	0.3	0.0	0.2	0.2
Stearine	12.8	6.5	48.4	30.3	1.9	97.2	13.3	27.6	14.2	5.5	1.7	0.0	0.0
HW SBO	10.5	4.4	42.0	40.0	2.9	109.5	9.1	–7.5	0.9	0.0	0.1	0.0	0.0
Margarine oil ^b	11.3	13.6	75.2	0.0	0.0	64.7	39.7	41.3	73.7	54.1	44.7	22.3	3.3
Shortening oil ^c	11.3	5.1	72.6	11.0	0.0	81.5	31.8	29.3	36.3	13.7	4.6	0.0	0.0

^a160°C, 40 psi H₂ pressure, 0.02% nickel; ^b216°C, 20 psi H₂ pressure, 0.03% nickel; ^c221°C, 20 psi H₂ pressure, 0.03% nickel

2 at 33.3°C; stick products 20–25 at 10°C, 10–12 at 21.1°C, and 2–4 at 33.3°C. The hydrogenated soybean oil, when blended with 25–50% liquid oil, results in SFCs suitable for tub and stick products, respectively. The melting point of the blended oils will usually be 32–35°C. The *trans* isomer content of the basestock is about 40%, which, after blending, yields final *trans* values for tub and stick products of 10 and 20%, respectively. *Trans*-containing triglycerides are very sharply melting materials at low temperatures. They provide functionality for spreadability and resistance to oil-off at room temperatures, yet they melt very quickly at body temperature to yield a pleasant, cooling sensation in the mouth.

Shortening Basestock and Formulation of Shortening

Shortening basestocks are typically prepared by hydrogenation of soybean oil to an IV of about 80. Lower temperatures and higher pressures are used than for margarine basestocks.

To formulate shortenings, liquid oil is blended to decrease the SFC, and addition of completely hydrogenated hardstock (10–12%) raises the 33.3°C and 40°C SFC values.

The baking industry employs a number of shortenings. Their *trans* acid content varies from about 12% to nearly 25%. Reduction in the *trans* acid content of shortenings is possible by alternative processing techniques such as interest-erification. However, no- and low-*trans* shortenings, while equivalent in performance to hydrogenated products, may be more expensive and will have elevated saturated acid contents.

High-Stability Oils

High-stability oils (HSOs) were developed more than 30 years ago (Gooding, 1972). Compared to commodity oils (soybean, corn, cottonseed, canola, peanut), they are expensive, but they are extremely stable and fill definite needs for the food industry. They are liquids at ambient temperature and perform well as spray oils and in products with large surface areas or where long shelf life is required.

HSOs are at least four times more resistant to oxidation and hydrolysis than commodity salad oils; this translates into slower development of off-flavors and marked improvement in color stability. Typical applications include use as carriers of flavors, moisture barriers, viscosity modifiers, gloss enhancers, lubricating/releasing agents, and anti-dusting agents, as well as use in roasting of nuts and frying operations.

Use in 2000 was estimated to be 45,000–57,000 metric tons—70% low-end HSO, 10% mid-range, and 20% high-end. These designations refer to their relative stability under active oxygen method conditions (100°C) or hours to reach a peroxide value of 100. Low, mid-range, and high-end oils have peroxide values of 50–100, 100–300, and >300, respectively (Lampert, 2000).

HSOs can be processed from both commodity oils and oils that have been modified genetically or by plant breeding. High-oleic corn, soybean, and sunflower oils meet requirements for low-end HSO without processing beyond refining, bleaching, and deodorizing, whereas soybean oil requires partial hydrogenation and dry fractionation as well. Both medium- and high-end HSOs can be prepared from both commodity oils and oils modified by either genetic engineer-

ing or plant breeding. However, light, partial or heavy hydrogenation and dry fractionation must be employed along with the usual refining, bleaching, and deodorization steps.

Low-end HSOs prepared from hydrogenated, dry-fractionated soybean oil contain 15% saturates and 32% *trans*, whereas high-oleic sunflower oil contains 9.5% saturates and 1% *trans*. HSOs based on canola and high-oleic canola oils offer opportunity for *trans* reduction in mid-range applications. Canola HSO shows 18–29% *trans*, compared to 51% for soy-based oil. Similarly, high-oleic-based, high-end oils have 33% *trans* compared to 48% for cottonseed- or soybean-based oils (Lampert, 2000).

HSOs are liquids at ambient temperature and are highly functional and convenient to use. They are used at low levels, often 0.2 and 1%, and are most commonly sprayed onto the surface of the food or ingredient. Although more expensive than commodity oils, processing costs are reduced, making final pricing comparable.

It is expected that increased use of HSOs will occur in the future to reduce the fat content in foods, improve shelf life, and improve health and nutrition.

Canola Oil

Hydrogenation of canola oil has been studied extensively in the laboratory (see review by Koseoglu and Lusas, 1990). Although canola oil is widely used in margarines/spreads and shortenings, the *trans* isomer content of these products tends to be somewhat higher than soybean-based products (Postmus et al., 1989).

Compared to soybean oil, hydrogenation of canola oil results in more *trans* acids at a given IV level. For example, canola oil (IV 113), when hydrogenated to IV 80 for shortening stock, contains about 45% *trans* acids, compared to 31–32% for soybean oil at the same IV. Canola margarine stock (IV 75) contains 50% *trans*, compared to 40% for soybean oil at IV 65. Lightly hydrogenated canola (IV 90) used as a frying fat contains 20% *trans*, whereas soybean oil at IV 110–116 contains

about 10–12% *trans* (Eskin et al., 1996).

These phenomena can be accounted for by the differences in fatty acid composition of the two oils. Canola oil contains 60% oleic acid and about 32% polyunsaturated acids (22% linoleic acid and 10% linolenic acid), whereas soybean oil contains about 22% oleic acid and 63% polyunsaturated acids. Thus, the high content of oleic acid renders canola oil more amenable to isomerization/*trans* fatty acid formation during hydrogenation; also sulfur-containing glucosinolates found in canola oil tend to poison the catalyst, thus promoting formation of *trans* acids. Canola oil tends to crystallize in the undesirable beta (highest-melting) form because of the low levels of palmitic acid found in the oil. To improve the crystal habit, the addition of palm oil prior to hydrogenation reportedly stabilizes the oil in the desirable beta-prime form desired for margarines and shortenings (Eskin et al., 1996).

Cottonseed Oil

Cottonseed oil has an IV of about 110 and contains about 25% saturated acids. A basestock system for formulation of shortenings, margarines, and spreads consists of five hydrogenated oils along with a hardstock or completely hydrogenated component (IV >5). Oils hydrogenated to an IV of 75–80 under non-selective conditions (350°F, 30–45 psi, 0.02% nickel catalyst) possess flat solid fat index (SFI) curves suitable for shortenings, whereas the IV 58, 65, and 70 oils hydrogenated under selective conditions (440°F, 11–15 psi, 0.04–0.08% nickel catalyst) possess steep SFI curves needed for margarine/spreads. The IV 58 oils have SFIs and melting properties very similar to those of IV 65 soybean oil and are similar in *trans* acid content. In 1997, only 8 million lb of cottonseed oil was used in margarines/spreads in the U.S.

O'Brien and Wan (2001) provide an excellent review of food uses and processing of cottonseed oil.

Corn Oil

During 1955–85, corn oil usage in margarines/spreads increased from less than 500,000 lb to 210 million lb, but dropped to about 61 million lb by 1997. Corn oil contains about 13% saturated acids and has an IV of approximately 127. Soft and stick margarines

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formulated from blends of hydrogenated soybean oil and liquid corn oil are available commercially.

Soybean oil basestocks are produced by hydrogenation of the oil to IVs of 65–67 under selective conditions and contain about 48% *trans* acids. The IV 65 oil blended with 25–30% liquid corn oil is suitable for soft products, while the IV 67 oil blended with 45–47% liquid corn oil is suitable for stick products. The *trans* acid content of soft and stick products is 12–14% and 20–24%, respectively.

Strategies to Reduce *trans* Acids

There are a number of strategies to reduce the *trans* fatty acid content of oils:

- **Interesterification.** The patent literature is replete with information on interesterification as a route to low-*trans* fats and oils. Gillies (1974) covered the patent literature from 1960 to 1974. A further search of the patent literature using margarine/shortening and interesterification as key words yields more than 46,000 references since 1976 alone. Thus, a comprehensive review would not be practical. Instead, several examples will be given from the author's laboratory.

Random interesterification of 80% liquid soybean oil with 20% completely hydrogenated soybean oil provides a route to soft margarine oil having suitable solid fat and crystal structures (List et al., 1977). Further work in which the interesterified oils were formulated into soft margarines in the pilot plant demonstrated that the 80:20 blend produced margarine that was harder and more difficult to spread than hydrogenated controls. Adding 20% liquid oil resulted in a product with suitable spreadability, sensory properties, and resistance to oil/water loss (List et al., 1995a).

Random interesterification of other liquid oils, including corn, peanut, cottonseed, canola, and palm, with completely hydrogenated soybean or cottonseed flakes yields basestocks suitable for formulation of zero-*trans* margarines and shortenings (List et al., 1995b).

Shortening oils require higher, flatter SFI curves and higher melting points than margarine oils. To obtain these properties, it is necessary to incorporate more stearine into the interesteri-

fied blend. The desired SFIs and melting points are achieved by blending the interesterified basestock with additional liquid oil.

Typically, all-purpose shortening prepared from hydrogenated components show SFI values of 18–23, 14–19, 13–14, and 7–11 at 50, 70, 92, and 104°F, respectively. A 50:50 blend of interesterified and liquid soybean oil closely matches these values. Fluid shortenings can be prepared by blend-

ing 35% of the basestock with 65% soybean, corn, peanut, cottonseed, or canola oil.

- **Fractionation.** Rapid growth of the palm industry, beginning in the mid-1970s, prompted development of improved fractionation technology. Historically, solvent and detergent processes had been used, but today physical or dry fractionation is the standard industry method.

Palm oil (IV 51–53) is fractionated

into olein (IV 56–59) and stearine (IV 32–36) fractions. The olein fraction is further fractionated into mid-fractions, super oleins, and top oleins. The palm mid-fractions (IV 42–48) are further processed into harder fractions (IV 32–36). Fractionation of the stearine (IV 32–36) yields soft and super stearines (IV 40–42 and 17–21, respectively) (Tirtiaux, 1996). These fractions can be incorporated into margarines/shortenings and confectionery fats. However, replacing *trans* fat with highly saturated palm fractions will increase saturated acid content.

Further discussion of the fractionation process can be found in reviews by Krishnamurthy and Kellens (1996), Timms (1997), and Deffense (1985).

Palm Oil

Zero-*trans* margarine fats can be prepared via random interesterification of soybean oil with palm stearine or fully hydrogenated soybean oil in ratios of 80:20. Petrauskaite et al. (1998) concluded that increasing the amount of fully hydrogenated soybean oil to 30 parts produced zero-*trans* oils suitable for shortening; 40 parts palm stearine randomized with 60 parts soybean oil also produced shortening oil very similar to commercial products.

Ozay et al. (1998) described the formulation of *trans*-free margarines from sunflower and cottonseed oils interesterified with palm oil, palm kernel oil, palm stearine, and palm kernel olein and compared them to products made by simply

blending the components in various ratios. Palm oil crystallizes slowly compared to other fats and oils, leading to a phenomenon known as post hardening in which products become harder during storage. The authors observed minimal post hardening in their study and reported that the use of skim milk in preparing the emulsions prior to crystallization was effective in retarding post hardening in blends high in palm oil and palm kernel oil.

Yusoff et al. (1998) reported formulation of *trans*-free tub, pastry, and bakery margarines from palm oil, palm olein, palm stearine, and palm kernel olein interesterified with soybean and rapeseed oil. The normal level of palm oil in commercial soft tub products was reported to be 25%, but palm olein can be used up to a level of 40%.

Berger (1998) reported studies on palm oil usage in a variety of food products, including margarine, baking shortenings, frying fats, and dairy products such as whipped toppings, ice cream, cheese, and *vanaspati*, a butter-like product with a melting point of 37–38°C used extensively in India and Pakistan. *Vanaspati* is manufactured with a granular structure and a minimum of free oil at room temperatures. In the early 1980s, the product (1 million tons/year), produced in Pakistan from hydrogenated components, contained about 30% *trans* acids. After it was reformulated with 80% palm oil and 20% liquid vegetable oil, *trans* acids were reduced to less than 4%. However, the saturated acid content would be on the order of 40%.

Oils With Modified Composition

Over the past several decades, a number of oilseeds with modified fatty acid compositions have been developed and commercialized. Most have resulted from traditional plant breeding techniques (Lui, 1999; Gunstone, 2001; Loh, 2000; Wilson, 1999). These include high- and mid-level-oleic sunflower oil; high-oleic corn, soybean, and safflower oils; low-linolenic canola and soybeans oils; and high-oleic/low-linolenic canola oil.

A number of laboratory frying studies have demonstrated superiority of modified oils over commodity oils (Warner and Gupta, 2003; Warner and Knowlton, 1997; Warner et al., 1997; Mounts et al., 1994; Warner and Mounts, 1993, 1994; Su et al., 2003).

Although low-linolenic canola and soybeans oils have reached commercialization, costs and production problems have impeded their success in the marketplace. However, the new labeling regulations may provide new markets and demands for modified-composition oils.

Fluid Shortenings

Fluid shortenings are stable suspensions of 2–20% hard fat in liquid vegetable oil which may or not be hydrogenated (Herzing, 1996; Andre and Going, 1957; Holman and Quimby, 1950; Mitchell, 1950). Fluid shortenings have been used for many years in baked goods where high solids contents are not required, such as fillings, cakes, and breads. They serve the same function as solid shortenings by imparting tenderness and lubricity, as well as serving as carriers for emulsifiers needed for aerating cake batter or giving crumb strength to bread. Other advantages include the fact that, since they are liquid and pumpable, they can be easily metered into batch and continuous processes. Some reduction of *trans* acids might be achieved by substituting liquid or un-

hydrogenated oil in formulations where hydrogenated oils have been traditionally used.

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Physical and Chemical Properties of *trans*-Free Fats Produced by Chemical Interesterification of Vegetable Oil Blends¹

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ABSTRACT: Fat blends, formulated by mixing a highly saturated fat (palm stearin or fully hydrogenated soybean oil) with a native vegetable oil (soybean oil) in different ratios from 10:90 to 75:25 (wt%), were subjected to chemical interesterification reactions on laboratory scale (0.2% sodium methoxide catalyst, time = 90 min, temperature = 90°C). Starting and interesterified blends were investigated for triglyceride composition, solid fat content, free fatty acid content, and *trans* fatty acid (TFA) levels. Obtained values were compared to those of low- and high-*trans* commercial food fats. The interesterified blends with 30–50% of hard stock had plasticity curves in the range of commercial shortenings and stick-type margarines, while interesterified blends with 20% hard stock were suitable for use in soft tub-type margarines. Confectionery fat basestocks could be prepared from interesterified fat blends with 40% palm stearin or 25% fully hydrogenated soybean oil. TFA levels of interesterified blends were low (0.1%) compared to 1.3–12.1% in commercial food fats.

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KEY WORDS: Fat blends, interesterification, margarines, shortenings, *trans* fatty acids, vegetable oil.

Most native vegetable oils have only limited applications in their original forms due to their specific chemical compositions. To widen their use, vegetable oils are modified either chemically by hydrogenation or interesterification or physically by fractionation (1–4). Normally, hydrogenation is only done partially, depending upon required end-product quality. However, during partial hydrogenation, part of the *cis* double bonds are isomerized into their *trans* form. In the past, formation of *trans* isomers [*trans* fatty acids (TFA)] was considered an advantageous side-reaction because TFA have higher melting points and greater stability than *cis* fatty acids (5). Basestocks used for formulation of margarines in the United Kingdom contain 11–39% TFA, those in Western and Eastern

Europe contain 7–32%, and those in North America contain 22–45% TFA (1,6,7).

In the past few years, several nutritional studies have suggested a direct relationship between TFA and increased risk for coronary heart disease (8–11). As a consequence of this controversy about TFA, a trend is observed in the food industry to replace partially hydrogenated oils by other fat sources with lower *trans* contents. Recent literature data show that fully hydrogenated oils are used for the manufacture of low- to zero-*trans* commercial fats (12).

Intesterification is one of the alternatives to the partial hydrogenation process that can be used to give fats and oils desired functionality. It has been applied for many years to modify the physical properties of lard (13). Interesterification of blends of fully hydrogenated vegetable oil with a liquid oil has been used to produce a zero-*trans* solid fat with the desired physical properties (14–17).

The aim of this study was to assist in the proper choice of oils to produce a zero-*trans* hard fat phase with melting characteristics similar to commercial fats. Changes in triglyceride (TAG) composition and melting behavior during the interesterification of blends of a highly saturated fat (palm stearin or fully hydrogenated soybean oil) with a native vegetable oil (soybean oil) are presented. Interesterified hard stocks can be further fractionated to obtain the required products with low- to zero-*trans* isomer content.

EXPERIMENTAL PROCEDURES

Materials. Neutralized bleached soybean oil (SBO), fully hydrogenated soybean oil (FHSBO), and palm stearin (Pst) were obtained from De Smet Group, Edegem, Belgium. Sodium methoxide was provided by HULS, Halle, Belgium. Commercial tub and stick margarines were purchased locally. All fats and oils were stored below 0°C until analysis.

TAG standards were purchased from Sigma Chemical, Bornem, Belgium. Acetonitrile and acetone were high-performance liquid chromatography (HPLC)-grade. Before use, they were filtered through a 0.45-μm filter.

Intesterification procedure. The fat blend (200 g), neutralized with 50% caustic soda solution, was dried for 40 min

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at 110°C and ca. 50 mbar. After lowering the temperature to 90°C, 0.2% sodium methoxide (powdered form) as catalyst was added. After 90 min of stirring, the mixture was cooled below 80°C. Vacuum was broken, and 20% citric acid solution was added to inactivate the catalyst, while the mixture was stirred mechanically for 15 min. Postbleaching was performed with 0.5% of bleaching earth (Tonsil 210 FF) under vacuum for 30 min at 90°C.

Analytical procedures. Solid fat content (SFC) was determined with a Bruker Minispec pulsed nuclear magnetic resonance (pNMR) analyzer Model No. 20 (Karlsruhe-Forchheim, Germany). The fat was melted at 80°C and placed in an ice-bath (0°C) for 60 min before the first SFC measurement. Before measuring, the samples were conditioned for 30 min at the desired temperature. The capillary melting point was determined by AOCS Official Method Ce 1-25 (18). Fatty acid methyl esters (FAME) were prepared and subsequently analyzed with a Carlo Erba 5160 gas-liquid chromatograph, equipped with a flame-ionization detector and a split injector (Carlo Erba, Milano, Italy), as described in AOCS Official Methods Ce 1-62 and Ce 2-66 (18). A fused-silica capillary column, coated with 100% cyanopropyl polysiloxane (CPTM, Sil 88, 50 m × 0.25 mm internal diameter, 0.25 µm film thickness, Chrompack, Bergen op Zoom, The Netherlands), was used with helium as a carrier gas. For TFA determination, temperature was programmed as described in AOCS Official Method Ce 1c-89 (18). Initial oven temperature was set at 150°C and increased at a rate of 1.3°C/min to 200°C, where it was held until completion of the analysis. Injector and detector were maintained at 250°C. Identification of the individual *trans* isomers was realized with pure TAG standards and elaidinized linseed oil FAME, prepared as described elsewhere (19), as reference compounds. Quantitative analyses were performed with a Shimadzu RC3A (Kyoto, Japan). Iodine values (IV) were determined directly from the fatty acid (FA) compositions by AOCS Official Method Cd 1c-85 (18). Free fatty acids (FFA) were determined by AOCS Official Method Ca 5a-40 (18).

The TAG composition was analyzed in a reversed-phase high-performance liquid chromatograph (RP-HPLC) (Gilson, France) on an Allsphere ODS-2 column (3 µm, 150 × 4.6 mm; Alltech, Laarne, Belgium) with acetonitrile-acetone (37:63, vol/vol) as the eluent at a flow rate of 1 mL/min, and a refractive index detector. The equivalent carbon number (ECN) method was used to predict the elution order of TAG on RP-HPLC. Individual peaks were identified by comparing the retention time with that of reference TAG. Vegetable oils were solubilized in solvent mixture at 20 mg/mL and injected in the quantity of 20 µL. Random TAG distributions were calculated from FA compositional data [AOCS Official Method Ce 5b-89 (18)].

RESULTS AND DISCUSSION

The physical and chemical characteristics of the starting materials are presented in Table 1. Pst and FHSBO were both

TABLE 1
Physical and Chemical Characteristics of Palm Stearin,
Fully Hydrogenated Soybean Oil, and Soybean Oil^a

Feedstock	m.p. (°C)	IV (g I ₂ /100 g)	PUFA/ SFA	TFA (%)
SBO	—	144.1	5.5	0.1
Pst	56.5	26.0	0.4	0.1
FHSBO	71.0	0.8	—	0.1

^am.p., melting point; IV, iodine value; PUFA/SFA, ratio of polyunsaturated and saturated fatty acids; TFA, *trans* fatty acids; SBO, soybean oil; Pst, palm stearin; FHSBO, fully hydrogenated soybean oil.

used as hard stocks. Pst, compared to FHSBO, had a lower melting point and higher IV. Small amounts of TFA (0.1%) were detected. According to literature data, starting materials can contain up to 2.1% of TFA (16). TFA in SBO and Pst are formed during deodorization or physical refining. TFA in FHSBO are minor side components formed during hydrogenation.

Good catalyst activity results in a clear increase in FFA. Theoretically, addition of 0.2% catalyst leads to the formation of 1.0% soap and 1.0% FAME. The soaps are converted to FFA during catalyst inactivation, while the FAME remain unchanged. Both volatile compounds are removed during deodorization and are effective losses. An increase in acidity from 0.1 to 1.0% was observed in all interesterified fat blends.

Randomization induced changes in TAG composition of the fat blends. In Tables 2 and 3, experimentally determined TAG compositions of Pst/SBO and FHSBO/SBO blends are compared with the calculated random distribution. TAG types are summarized according to the degree of unsaturation: U₁, U₂S, and S₃ (U₁ = triunsaturated, U₂S = diunsaturated, S₃ = trisaturated). Monounsaturated (S₂U) can be calculated by subtraction (S₂U = 100 - U₁ - U₂S - S₃). After interesterification, the high proportions of S₃ present in the starting blends were reduced 73–89%. Furthermore, interesterification resulted in a decrease of U₁ and formation of U₂S. The greatest changes were observed for the blends with 40–50% hard stock (a relative decrease of U₁ of 38–40% and 54–64%

TABLE 2
Triacylglycerol Class^a of Fat Blends of Palm Stearin and Soybean Oil
Before (B) and After (I) Interesterification and Calculated (C)
According to Random Distribution Hypothesis

Fat blend (Pst/SBO) ^b wt%	Triacylglycerol ^b (mol %)								
	U ₁			U ₂ S			S ₃		
	B	I	C	B	I	C	B	I	C
10:90	51.9	51.1	49.5	27.1	30.9	39.2	38.2	0.9	0.9
20:80	49.8	39.4	37.0	25.8	33.1	43.6	21.9	3.7	2.3
30:70	45.5	33.1	28.3	24.0	34.2	44.4	10.7	4.3	4.1
40:60	37.2	23.0	21.0	19.3	31.6	43.0	18.5	6.3	6.7
50:50	35.0	21.0	14.3	18.4	29.3	39.2	47.7	10.4	10.9

^aDetermined by reversed-phase high-performance liquid chromatography with refractive index detector.

^bFatty acids in triacylglycerol: U, unsaturated; S, saturated.

^cPst/SBO, blend of palm stearin and soybean oil.

Crystallization Kinetics of Palm Stearin in Blends with Sesame Seed Oil

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ABSTRACT: This study investigates the crystallization kinetics of palm stearin (PS), a palm oil fraction, in blends with sesame seed oil. The results indicate that the crystallization behavior of PS in sesame oil is mainly associated with the crystallization of tripalmitin. Therefore, crystallization of blends of 26, 42, 60, and 80% (wt/vol) PS in sesame oil was described by equations developed for simpler systems (e.g., Fisher and Turnbull equation). The isothermal crystallization, melting profile, and fitting of the kinetics of nucleation to the Fisher and Turnbull equation showed that the 26, 42, and 60% PS/sesame oil blends crystallized mainly in the β_1 polymorph state. In contrast, the 80% blend crystallized in two different polymorph states (i.e., β_1 at $T \leq 307.6$ K and β_2 at $T \geq 308.2$ K). The data indicated that, in spite of the higher concentration of PS in the 80% PS/sesame oil system, crystallization in the β_1 state required more free energy for nucleation (ΔG_c) than β_1 crystallization in the 26, 42, and 60% PS/sesame oil. At the low cooling rate used (1 K/min) it was observed that, for a particular PS blend, the higher the effective supercooling the higher the viscosity of the oil phase and the smaller the induction time of crystallization (τ_i). Additionally, the β_1 crystals from PS developed at the highest effective supercooling investigated, were smaller than the β_1 crystals obtained at lower effective supercooling.

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KEY WORDS: Avrami, crystallization, Fisher-Turnbull, oil viscosity, palm oil, palm stearin.

Sesame (*Sesamum indicum* L.) is an important annual oilseed crop in developing countries. India, China, Sudan, Mexico, and Burma produced approximately 60% of its global production for the period 1987–1991 (1,2). Sesame oil, conventionally extracted by pressing roasting seeds without further refining, has a mild, pleasant, and unique taste with remarkable oxidative stability. The fatty acid composition, triacylglyceride distribution, concentrations of sterols, tocopherols and lignins in the oil, and the effect of several processing conditions on its oxidative stability have been studied (1,3–7).

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Nowadays consumers are demanding edible oils devoid of any chemical treatment and with natural characteristics and natural flavor. As a consequence, the market for novel oils that are cold-press extracted and that possess natural oxidative stability has been developing worldwide during the last few years. Sesame seed oil fulfills most of these characteristics and is now marketed in industrialized countries, mainly as a gourmet salad oil with unique flavor. However, additional value-added products like margarine, spreads, and squeezable spreads based on sesame oil have not been developed. These products require a solid-to-liquid ratio with the appropriate melting profile to obtain the texture and functionality (i.e., spreadability) desired by consumers. However, the natural triglyceride composition of sesame oil is highly unsaturated, consisting of 7–12% palmitic, 3.5–6% stearic, 0.09–0.29% palmitoleic, 39–43% oleic, 40–44% linoleic, and 0.40–0.85% linolenic acids (1,8). Using differential scanning calorimetry (DSC), Dibildox-Alvarado and Toro-Vazquez (8) determined the crystallization exotherm for triglycerides in sesame oil with an onset at around -2.5°C and a maximum at around -7°C . Thus, the development of a functional solid phase in sesame oil without the use of chemical processes, such as hydrogenation and interesterification, is not an easy task.

Several processes are used to modify the phase change properties of vegetable oils and improve their plasticity, and therefore, the versatility for use by the food industry. The most utilized processes are hydrogenation and interesterification (9). However, hydrogenation of the naturally occurring *cis* unsaturated fatty acids (i.e., oleic, linoleic, and linolenic fatty acids) produces *trans* fatty acids. Consumer concern associated with the atherogenic effects of *trans* fatty acids limits the future of this process as a way to modify the solid-to-liquid ratio in vegetable oils. In fact, more *trans*-free spreads (e.g., obtained without hydrogenation) are being introduced successfully into the market. This trend is expected to continue as the proposal of the U.S. Food and Drug Administration to specify *trans* fatty acid content in food product labels proceeds (10). On the other hand, chemical or enzymatic interesterification processes, technologies utilized mainly in European countries, have particular drawbacks that are mainly associated with the yield efficiency and cost of the processes (11). In these processes, a high-melt

ing temperature fraction (i.e., palm stearin (PS), full or partially hydrogenated oils) is interesterified with a particular vegetable oil in the manufacture of *trans*-free margarine and vegetable shortening (12,13).

An additional alternative involves the direct blending of a high-melting-temperature fraction with a vegetable oil (i.e., sesame oil). This last process has the additional advantage that no chemical process is involved, consistent with the consumer trend toward natural products. The aim of this study was to investigate the crystallization kinetics of PS, a palm oil fraction constituted mainly by triglycerides of high-melting temperature, in blends with sesame seed oil. This process constitutes a feasible alternative to expand the use of sesame oil through the development of value-added products such as squeezable margarines, spreads, or low-fat margarines. According to the National Association of Margarine Manufacturers, the consumption of margarine-type products grew from 2.6 to 9.1 pounds per capita for the period between 1930 and 1996 (10). In contrast, butter consumption dropped from 17.6 to 4.3 pounds per person (10).

PS is obtained through fractional crystallization of refined, bleached, and deodorized palm oil (12). Tripalmitin (TP) is the triglyceride with the highest melting temperature in both palm oil (5–10% w/w) and PS (12–56% w/w), depending on the fractionation temperature (14). As a consequence, TP should affect crystallization kinetics and polymorphic behavior of palm oil and PS. Our previous research (8,15) on crystallization has indicated that solutions of pure TP in sesame oil behave like binary solutions formed by saturated triglycerides (i.e., TP) and unsaturated triglycerides (i.e., sesame oil). In the present study, we evaluate whether this behavior holds in a more complex crystallization system, i.e., mixtures of PS in sesame oil.

MATERIALS AND METHODS

Materials. Whole-seed refined sesame oil was obtained from a local company (DIPASA de México, Celaya, Gto., México). The oil was stored at 4°C in the dark. The same batch was used in all the experiments.

Pure TP (>99% pure, experimentally confirmed by gas chromatography and DSC) was obtained from Sigma Chemical Co. (St. Louis, MO). Refined, bleached, and deodorized PS was provided by the Palm Oil Research Institute of Malaysia (Kuala Lumpur, Malaysia). Both TP and PS were used without further purification.

Chemical analysis. The fatty acids composition of sesame oil and PS was determined by gas chromatography utilizing a Shimadzu chromatograph GC-9A (Shimadzu Corp., Kyoto, Japan) with flame-ionization detector and a Supelco (Bellefonte, PA) glass column (2.6 m × 2.1 mm) packed with GP 10% SP 2330 on Chromosorb 100/120. The analysis conditions have been previously reported (8).

The triglyceride profile for PS was determined by high-performance liquid chromatography (HPLC) following the conditions described previously by Che Man *et al.* (14) utilizing a

Waters 600 E instrument (Waters Millipore Co., Milford, MA) with a refractive index detector and a Nova Pack C₁₈ column (3.9 × 300 mm) (Water Millipore Co.). Triglyceride peaks were assigned based on the retention time of triglyceride standards.

The particular concentration of TP in PS was determined by gas chromatography of the saturated triglyceride fraction isolated by silver ion thin-layer chromatography (TLC) following the conditions described by Nikolova-Damyanova (16).

DSC. A PerkinElmer differential scanning calorimeter (model DSC-7; PerkinElmer, Norwalk, CT) equipped with a dry box was used in all cases. The temperature calibration of the equipment was done with indium (onset temperature for melting = 429.8 K) and *n*-hexatriacontane (onset temperature for melting = 349.3 K), and the baseline was developed with an empty aluminum pan. The calibration for heat involved in phase changes (i.e., melting/crystallization) was made only with indium (ΔH for melting = 28.45 J/g).

Nonisothermal DSC analysis. For dynamic runs, ~12 mg of TP solution in sesame oil (0.00, 0.32, 0.98, 1.80, 2.62, 10, and 25% wt/vol) or PS blend in sesame oil (0.00, 26, 42, 60, and 80% wt/vol) was sealed in a pan and held at 353 K for 30 min before each DSC scan. The system was cooled at a rate of 10 K/min until a temperature of 243 K was achieved. After 2 min at this temperature, the melting curve was obtained by heating the system at 5 K/min until reaching 353 K. The temperature in the maxima of both the exothermal peak of crystallization (T_c) and the endothermal melting peak (T_m) were calculated using the DSC-7 software library. In the same way, the heating and cooling thermograms of pure TP and PS were determined.

The ideal behavior of the TP crystallization/melting in both systems, TP/sesame oil and PS/sesame oil, was evaluated using the Hildebrand equation (17):

$$\ln(x) = \Delta H_f / R (1/T_m - 1/T_p) \quad (1)$$

where ΔH_f is the enthalpy of fusion per mole of pure TP, T_p and T_m are the melting temperature of pure TP and in the oil solutions, respectively (i.e., the temperature in the peak maximum in the DSC endotherm), x is the mole fraction of TP in the system (i.e., TP/sesame oil and PS/sesame oil solutions), and R is the universal gas constant. An average molecular weight for sesame oil triglycerides (874.93) and PS triglycerides (842.15) was calculated from the fatty acid composition.

Isothermal DSC analysis. The PS/sesame oil solution (26, 42, 60, and 80% wt/vol) was heated at 353 K for 30 min and then cooled (1.0 K/min) to a preset temperature (297.5–309 K) and held at that temperature for crystallization. After complete crystallization, the system was left at the isothermal temperature for additional 35 min. Afterward, the melting thermogram was obtained by heating the system at a rate of 1.0 K/min. The induction time for crystallization (T_i) was calculated from the isothermal thermogram as the time from the start of the isothermal process to the beginning of crystallization (i.e., time where the heat capacity of the sample had a significant departure from the baseline) using the DSC-7 software library. The cooling rate was selected according to conditions used in previous stud-

ies involving isothermal (8) and nonisothermal (15) TP crystallization in sesame oil. This cooling rate is in line with the slow cooling rate achieved by industrial crystallizers.

Microscopy studies. Crystal morphology of the PS/sesame oil solution was obtained under the same isothermal conditions utilized in the DSC studies using a polarized microscope with camera (model BX60F/PMC35; Olympus Optical Co., Ltd., Tokyo, Japan). The experimental setup has been described previously (8). After induction of nucleation, pictures of the crystals were taken as a function of time.

Calculation of kinetic parameters. The isothermal DSC data were utilized to evaluate the kinetics of TP crystallization in the PS/sesame oil solutions using the Avrami equation (18):

$$-\ln(1 - F) = zt^n \quad [2]$$

where F is the fraction of crystal transformed at time t , n is the index of the crystallization reaction or Avrami exponent, and z is the rate constant of crystallization, which depends on the magnitude of n , the nucleation rate, and the linear growth rate of the spherulite (19). The value of F was calculated by integration of the isothermal DSC crystallization curves as described by Henderson (20) utilizing Equation 3 and according to Figure 1:

$$F = \Delta H_t / \Delta H_{\text{tot}} \quad [3]$$

where ΔH_t is the area under the DSC crystallization curve from $t = T_i$ to $t = t$, and ΔH_{tot} is the total area under the crystallization curve. The values of ΔH_t and ΔH_{tot} were calculated with the DSC software library. In fact, F is a reduced crystallinity since it associates an instant crystallinity to the total one achieved

under the experimental conditions. Then, F varies from 0 to 1.

The value of n was calculated from the slope of the linear regression of the plot of $\ln[-\ln(1 - F)]$ vs. $\ln(t)$ using values of fractional crystallization between 0.25 and 0.75 (18). The n value describes the crystal growth mechanism. Thus, a crystallization process with a $n = 4$ follows a polyhedral crystal growth mechanism, a value of $n = 3$ represents a plate-like crystal growth mechanism, and a $n = 2$ indicates a linear crystal growth (19).

When nucleation occurs from the melt the rate of nucleation, J , depends on the activation free energy to develop a stable nucleus, ΔG_c , and the activation free energy for molecular diffusion, ΔG_d . The Fisher-Turnbull equation (Eq. 4) describes this situation and was utilized, according to Ng (21) and Herrera *et al.* (22), to evaluate the magnitude of ΔG_c

$$J = (NkT/h)\exp(-\Delta G_c/kT)\exp(-\Delta G_d/kT) \quad [4]$$

where J is the rate of nucleation that is inversely proportional to τ_p , N is the number of molecules per mole, k is the Boltzman constant, T is absolute temperature, and h is Planck's constant. In a spherical nucleus, ΔG_c is associated with the effective supercooling, ΔT , and the surface free energy at the crystal/melt interface, σ , through the following equation:

$$\Delta G_c = (16/3)\pi\sigma^3(T_M^o)^2/(\Delta H)^2(\Delta T)^2 \quad [5]$$

where $(16/3)\pi$ results from the spherical shape attributed to the nucleus and ΔH is the heat of fusion. The effective supercooling, $(T_M^o - T)$, is the difference between the equilibrium melting temperature, T_M^o , and the isothermal temperature of crystallization, T . The magnitude of T_M^o was established following

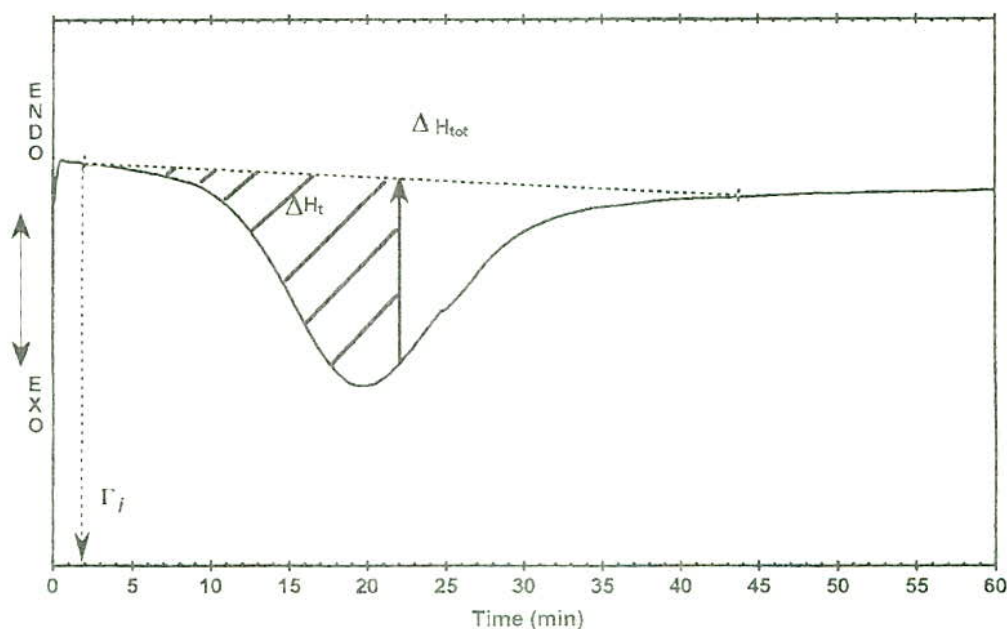


FIG. 1. Determination of reduced crystallinity, F , from exotherm obtained at isothermal conditions.

the procedure described by Hoffman and Weeks (23). Thus, the relationship between T and the apparent melting temperature of TP in the PS/sesame oil solutions (T_M') was established plotting T_M' vs T . The T_M' value was determined from the melting thermograms (heating rate of 1 K/min) after the corresponding crystallization according to the isothermal conditions described previously. Thus, the experimental T_M' vs. T plot provided a straight line whose crossing point with the line $T_M' = T$ represented T_M^0 (Fig. 2). The T_M^0 value is defined as the temperature where the smallest aggregation of molecules (i.e., unstable crystal nucleus) is in equilibrium with the molecules in the melt. This concept is particularly utilized in polymers (24). Thus, small aggregations of molecules without the correct tridimensional arrangement to develop a stable crystal nucleus will melt below T_M^0 . Finally, from the slope, s , of the linear regression of $\log[T_1 T]$ vs. $1/T(\Delta T)^2$ the calculation of ΔG_c was performed since $\Delta G_c = s k/(\Delta T)^2$.

Measurements of viscosity. The viscosity of the PS/sesame oil solution was determined under isothermal conditions at a shear rate of 15.82 s^{-1} utilizing a Brookfield LVDV-III viscosimeter (Brookfield Instruments, Stoughton, MA) with a cone and plate geometry with the cup CP-41. In all cases the volume of the sample was 0.5 mL and the temperature control was $\pm 0.1 \text{ K}$ (Brookfield TC-500).

The solution in the sample container of the viscosimeter was heated at 353 K for 30 min. Afterward, the system was cooled (1.0 K/min) until the desired temperature was achieved. The equilibrium time for the recording of the viscosity was 25 s.

The value of viscosity for each PS/sesame oil solution was plotted as a function of the effective supercooling and the T_1 .

RESULTS AND DISCUSSION

The fatty acid profile of the sesame oil and PS used are presented in Table 1. As previously indicated, sesame seed oil has a high degree of unsaturation, mainly provided by the high concentrations of oleic and linoleic fatty acids.

The triglyceride composition of PS was as follows, where M = myristic, P = palmitic, L = lauric, O = oleic, and St = stearic: MMM, 0.16 ± 0.01 ; MMP, 0.14 ± 0.01 ; MPL, 1.47 ± 0.11 ; PPP, 16.46 ± 0.17 ; PPO, 36.91 ± 0.12 ; PPSt, 3.39 ± 0.06 ; POSt, 31.21 ± 0.03 ; StOSt, 0.06 ± 0.02 ; OOO, 8.00 ± 0.11 ; and unknown, $1.58 \pm 0.77 \text{ wt\%}$. That is, the main constituents of PS were, in decreasing order of concentration, PPO, POSt, PPP, and PPSt, with TP as the triglyceride with the highest melting temperature (14,25). Thus, TP must affect the crystallization kinetics and polymorphic behavior of the PS/sesame oil solutions in a significant way. From the concentration of TP in the PS (16.46%), the effective TP concentrations for the 26, 42, 60, and 80% PS/sesame oil solutions were 4.27, 6.90, 9.85, and 13.14% (wt/vol), respectively.

The corresponding DSC cooling (Fig. 3) and heating (Fig. 4) dynamic thermograms pointed out the high degree of unsaturation of sesame oil. Sesame oil had a crystallization peak with a maximum at $\approx 256 \text{ K}$, a melting peak with maximum at $\approx 258.5 \text{ K}$, and melting was completed at $\approx 266 \text{ K}$. Although,

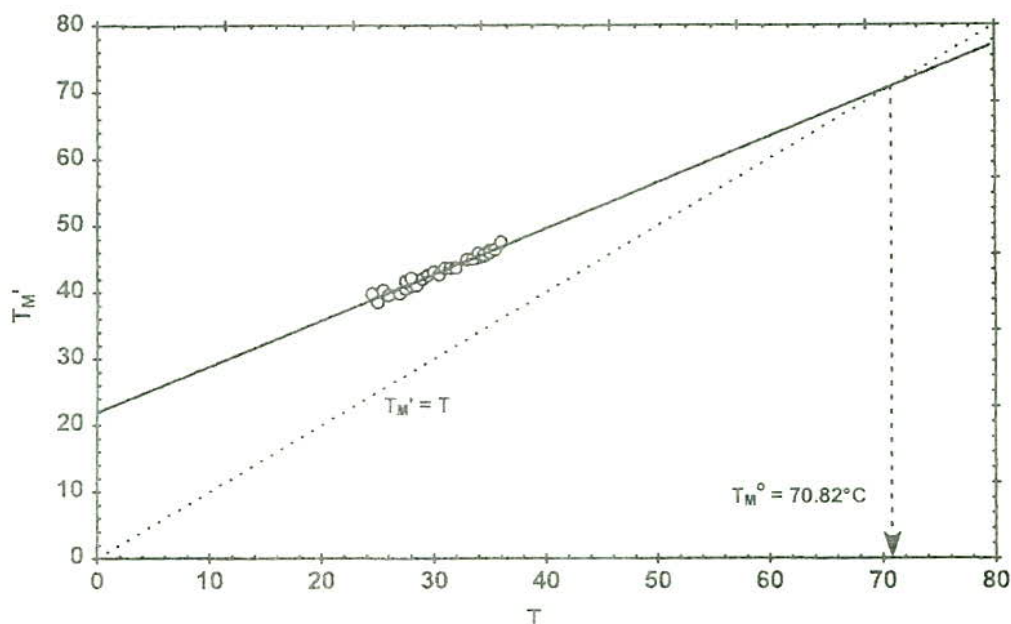


FIG. 2. Determination of the equilibrium melting temperature, T_M^0 , for palm stearin crystallization in sesame oil: T is the isothermal crystallization temperature and T_M' is the apparent melting temperature of the tripalmitin peak in the blends of palm stearin in sesame oil determined in the melting differential scanning calorimetry (DSC) thermograms (see Figs. 12 and 13).

TABLE 1
Fatty Acid Profile^a for Sesame Seed Oil and Palm Stearin (% wt/vol)

Fatty acid	Sesame oil			Palm stearin
	Present study	Ref. 9	Ref. 1	
Palmitic	9.87 ± 0.18	10.03 ± 0.21	9.35 ± 0.23	51.88 ± 1.88
Stearic	5.66 ± 0.05	5.71 ± 0.05	6.10 ± 0.37	4.67 ± 0.09
Palmitoleic	0.23 ± 0.04	0.28 ± 0.05	0.18 ± 0.04	ND ^b
Oleic	40.25 ± 0.21	40.14 ± 0.20	42.75 ± 1.14	33.66 ± 1.44
Linoleic	43.16 ± 0.14	42.70 ± 0.12	39.70 ± 1.28	8.05 ± 0.58
Linolenic	0.24 ± 0.01	0.61 ± 0.15	0.58 ± 0.04	0.42 ± 0.02
Cis-Vaccenic	ND	ND	0.85 ± 0.05	ND
Arachidic	ND	ND	0.30 ± 0.00	ND
Unknown	0.58 ± 0.05	0.64 ± 0.15	ND	1.37 ± 0.06

^aMean ± standard deviation ($n = 4$). ND, not determined.

the sesame seed oil thermograms were similar to the ones reported in our previous study (8), small differences in peak temperatures were observed. These differences mainly arise from the variation in the fatty acid composition between the sesame oils utilized in each study (Table 1) and from differences in the calibration procedure used in the DSC. In this study, a two-point (i.e., indium and *n*-hexatriacontane) temperature calibration was used, whereas in our previous report (8), a one-point (i.e., indium) calibration was performed. Therefore, the results reported here are more accurate.

The cooling thermogram for PS was quite simple with two crystallization peaks with maxima at 298.7 and 275.5 K, which corresponded to the highly saturated and unsaturated (i.e., olein fraction) triglyceride fractions, respectively (14,21). Based on the thermal and X-ray analysis of Busfield and Proschogo (26) and Swe *et al.* (27), the high-temperature endothermic peaks during the heating thermogram for PS were assigned to poly-

morphic states β_1' ($T_p = 311.1$ K) and β_1 ($T_p = 324.1$ K) (Fig. 4), while the low-temperature melting peak to polymorph states β_2' ($T_p = 275.8$ K) and α ($T_p = 281.1$). The β' crystal's size and shape produces good spreadability and plasticity to margarines and shortenings, since a fine crystal network is formed. However, some fats undergo a β' to β polymorph state transformation, which is induced by temperature fluctuations during storage. This results in products with hard consistency and sandy texture, since β crystals are bigger than β' crystals and have a higher melting temperature (8,28). Fats with high levels of C_{48} and C_{54} triglycerides are prone to β formation of crystals (i.e., PPP, OOO, StOSt, StStSt), as in hydrogenated canola and sunflower oils. In contrast, C_{50} (i.e., PPSt, PPO) and C_{52} (i.e., POST) triglycerides are strong β' formers (28), which explains the beneficial effect of palm oil and its derivatives (e.g., PS) in margarines and shortenings (29).

From the studies of Che Man *et al.* (14), and from experi-

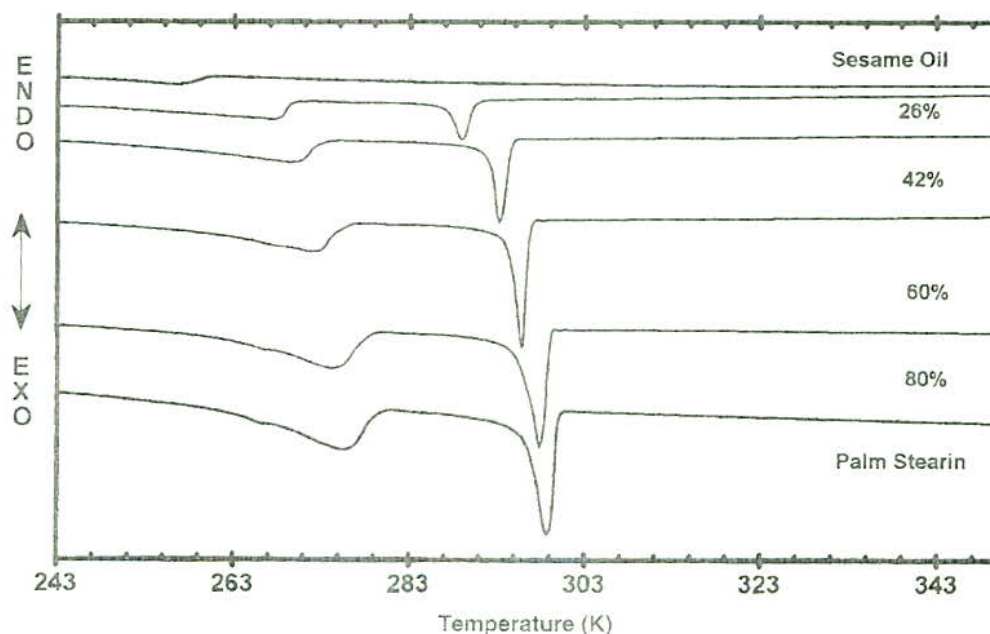


FIG. 3. Dynamic cooling thermogram (10 K/min) for sesame oil, palm stearin, and blends of palm stearin in sesame oil at different proportion.

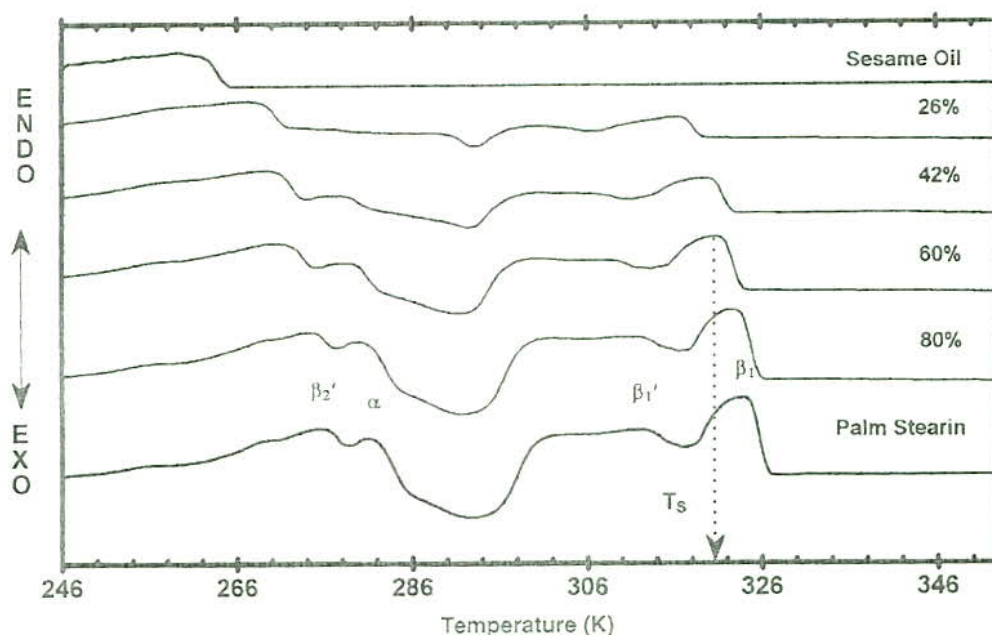


FIG. 4. Dynamic heating thermograms (5 K/min) for sesame oil, palm stearin, and blends of palm stearin in sesame oil at different proportion. T_s is the melting temperature of the tripalmitin peak. The polymorph states assigned to each endothermal peak are shown.

mental studies that involved the addition of pure TP to PS and PS/sesame oil solutions and further determination by DSC of the corresponding ΔH for crystallization and melting (data not shown), we established that the exotherm at 298.7 K corresponded to TP crystallization. The position of this peak shifted

to a lower temperature and broadened as PS was diluted with sesame oil (Fig. 3). As well, the melting events corresponding to the polymorphic states of the high- and low-temperature peaks (i.e., β_1' and β_1 , β_2' , and α , respectively), shifted to lower temperature and broadened as PS concentration decreased in

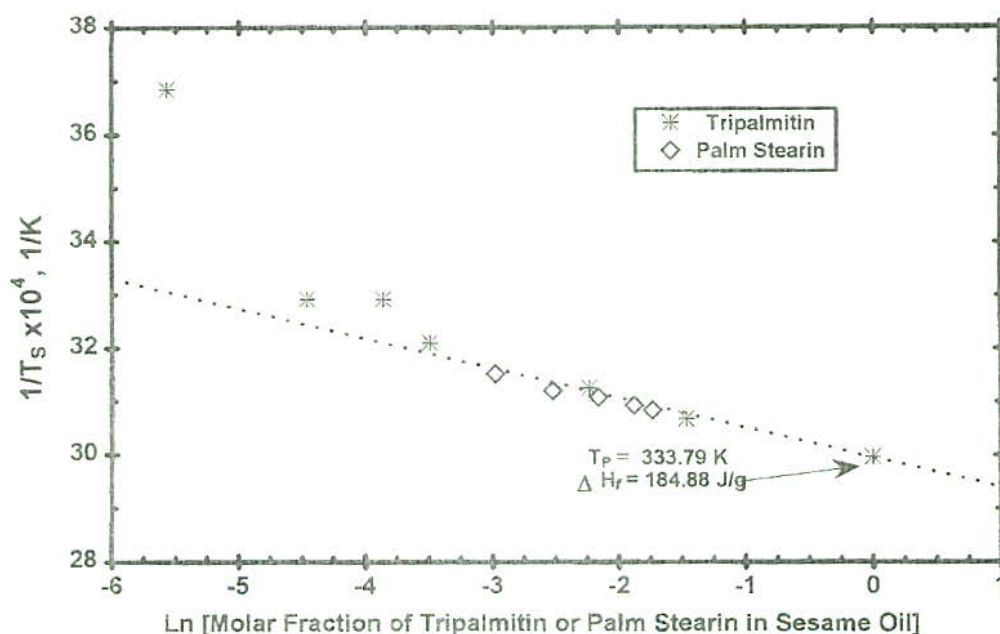


FIG. 5. Hildebrand plot for the blends of pure tripalmitin in sesame oil (0.32, 0.98, 1.80, 2.62, 10, and 25% wt/vol) and palm stearin in sesame oil (26, 42, 60, 80, and 100% wt/vol). T_p and ΔH_f are the experimental melting temperature and the molar enthalpy of fusion for pure tripalmitin, respectively.

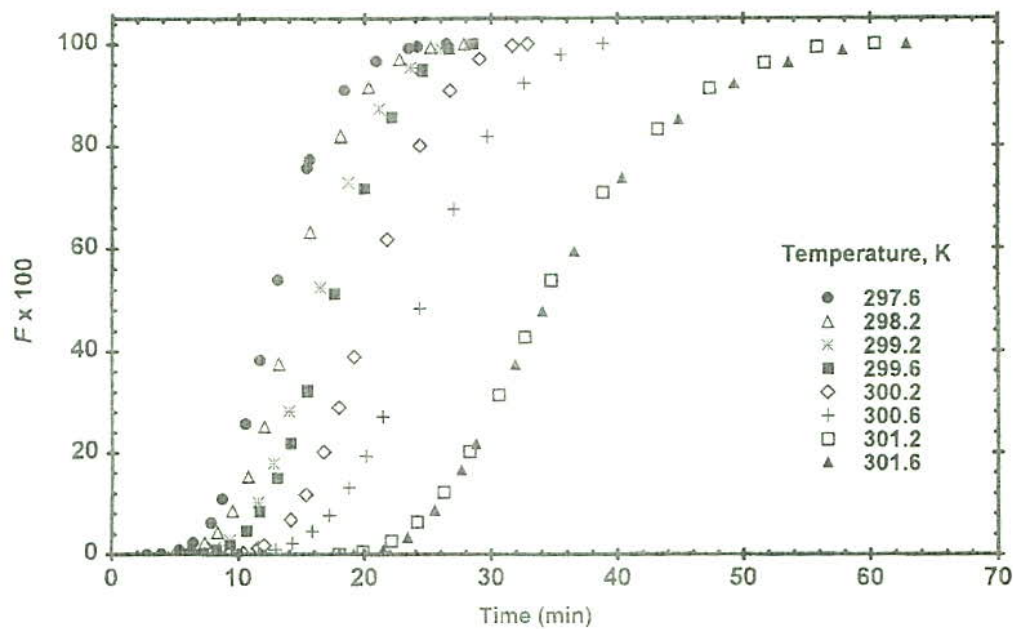


FIG. 6. Percentage of reduced crystallinity ($F \times 100$) as a function of time at different temperatures in the 26% palm stearin blend in sesame oil.

the blends (Fig. 4). The same trends were observed in solutions of pure TP in sesame oil (8), and this behavior was associated with solubility of TP in sesame oil. This can be appreciated in Figure 5, since our crystallization and melting data for the PS/sesame oil system fitted the Hildebrand equation very well. This relationship was also investigated for the TP/sesame oil system, also obtaining good agreement with the Hildebrand model as long as the TP concentration was higher than 0.98%. As indicated by Dibildox-Alvarado and Toro-Vazquez (8), at TP concentration lower than 0.98%, a high-melting-temperature triglyceride fraction of sesame oil could co-crystallize with TP and depress the melting point below the value predicted for pure TP. Then, within the concentrations of PS utilized in the sesame oil solutions, the fully saturated triglyceride fraction from PS (i.e., mainly TP) crystallized independently from sesame oil. Using reduced viscosity measurements in solutions of TP or tristearin in sesame oil, Toro-Vazquez and Gallegos-Infante (15) have shown that, prior to crystal nucleation, saturated triglycerides are segregated from the original lamellar organization of the unsaturated triglycerides in sesame oil.

The experimental T_p value for pure TP was 333.79 K with a ΔH_f of 184.88 J/g. These values are somewhat different from the ones determined previously by our group (8) under similar heating and cooling conditions ($T_p = 342$ K, $\Delta H_f = 185.37$ J/g) and by Norton's group (30) at a heating rate of 0.125 K/min ($T_p = 339.7$ K, $\Delta H_f = 204.37$ J/g). These differences might arise mainly for two reasons. First, as previously mentioned, a two-point calibration was used in the present study, whereas in previous reports (8,30) a one-point calibration was performed. In consequence, the results reported here are more accurate. Second, the shape of melting/crystallization curves and the behavior of polymorphic transformations are strongly affected by the

TABLE 2
Free Energy for Nucleation (ΔG_c) Index of Avrami (n), and Crystallization Rate Constant (z) for Palm Stearin Crystallization in Sesame Oil as a Function of Crystallization Temperature

Crystallization temperature (K)	Palm stearin (% wt/vol)	ΔG_c (kJ/mol)	Avrami parameters	
			n	$z \times 10^{-5}$ (min ⁻¹)
297.6	26	11.97	4.4	821.95
298.2		12.24	4.7	249.56
299.2		12.79	4.8	109.69
299.6		13.08	4.6	131.06
300.2		13.38	5.4	5.91
300.6		13.69	5.5	1.31
301.2		14.01	5.1	1.14
301.6		14.34	4.5	7.40
300.6	42	9.75	4.3	3095.43
301.2		9.98	4.0	5858.69
302.2		10.46	4.4	649.16
302.6		10.72	4.8	197.29
303.2		10.98	4.7	120.14
303.6		10.26	5.0	9.86
304.2		11.54	5.0	2.81
304.6		11.83	5.2	0.85
304.6	60	9.12	5.4	53.34
305.2		9.36	4.8	81.83
306.2		9.86	5.3	19.72
306.6		10.13	5.5	1.18
307.2		10.40	3.9	44.46
307.6		10.69	4.6	1.88
308.2		10.99	4.1	11.64
306.6	80	6.29	5.3	30.10
306.6		6.46	4.8	57.38
307.2		6.64	5.0	55.85
307.6		6.82	5.0	15.18
308.2		28.04	5.5	3.87
308.6		28.84	4.7	3.51
309.2		29.67	5.3	0.03

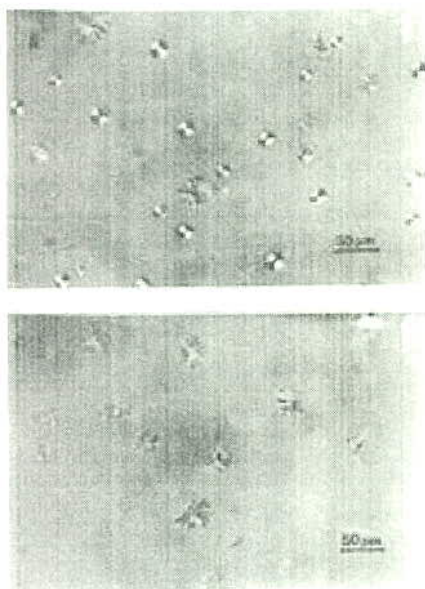


FIG. 7. Polarized light microphotographs of the crystals obtained with the 26% palm stearin (PS)/sesame oil solution at 297.6 K (6 min after τ_i , A) and 299.2 K (6.5 min after τ_i , B). τ_i , induction time of crystallization.

scan rate used during the DSC analysis (30). The Hildebrand equation obtained by linear regression using the experimental data for the 26, 42, 60, and 80% PS/sesame oil solutions [$1/T_S = 29.918 \times 10^{-4} - \ln(\text{molar fraction of PS in sesame oil})(0.531 \times 10^{-4})$] provided predictions for TP of $T_p = 334.25$ K and $\Delta H_f = 185.92$ J/g. These values are quite similar to the ones obtained experimentally by DSC measurements for pure TP.

The plot of the percentage of reduced crystallinity, $F \times 100$, as a function of time for the different PS/sesame oil solutions followed the same general behavior as shown for the 26% PS blend in Figure 6, i.e., increasing the rate of crystallization beyond the value of τ_i and then decreasing it until achieving zero crystallization rate at $F \times 100 = 100$. The values of n and z , the index of Avrami and the rate constant of crystallization, respectively, as a function of the crystallization temperature are shown in Table 2. A regression coefficient greater than 0.998 was always obtained for the linear regression of $\ln[-\ln(1 - F)]$ on $\ln(t)$. The coefficient of variation for replicate measurements was less than 6% for calculation of n and less than 8% for calculation of z . Values of n around 4 or greater were obtained in all cases. Similar magnitudes have been obtained by Metin and Hartel (31) in blends of cocoa butter with 5 and 10% of anhydrous milk fat (AMF) or solid fractions of AMF obtained by crystallization at 23, 28, 30, or 32°C. On the other hand, Kawamura (19) obtained values of n around 4 in palm oil crystallization. Based on the theory of crystallization of Avrami (18), values of n greater than 4 suggest heterogeneous nucleation and indicate the effect of sporadic nucleation on the development of new crystals. However, additional considerations associated with the effect of the cooling rate on the local-order (i.e., triglyceride lamellar organization), sporadic nucleation, and secondary crystallization must be taken into account in the determination of n values of triacylglyceride crystallization (Toro-Vazquez, J.F., Herrera-Coronda, V., Dibiddox-Alvarado, E., and Char'o-Alonso, N., unpublished results). Figures 7–9 are microphotographs of crystals developed in the 26% and 80% PS/sesame oil solution at different temperatures and crystallization time after the induction of crystallization (τ_i). TP is

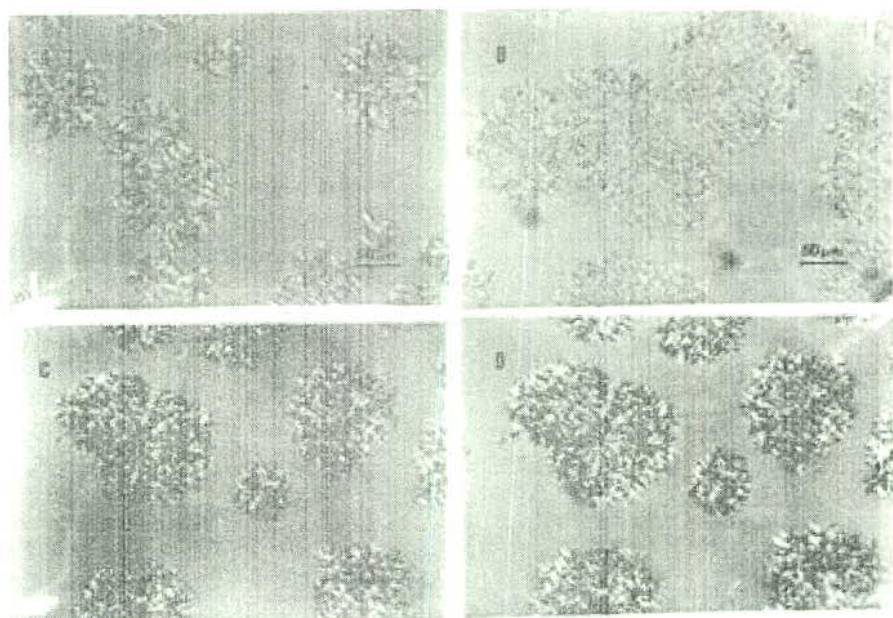


FIG. 8. Polarized light microphotographs of the crystals obtained with the 80% PS/sesame oil solution at 306.2 K (12 min and 20 min after τ_i , A and B, respectively) and 307.2 K (14 min and 20 min after τ_i , C and D, respectively). For abbreviations see Figure 7.

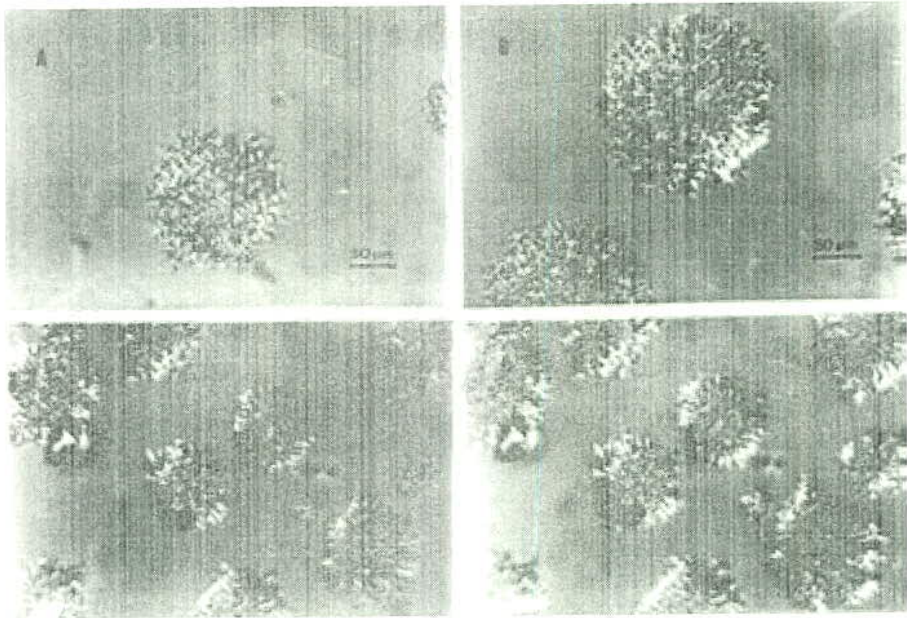


FIG. 9. Polarized light microphotographs of the crystals obtained with the 80% PS/sesame oil solution at 308.2 K (12 min and 20 min after τ_i , A and B, respectively) and 309.2 K (12 min and 20 min after τ_i , C and D, respectively). For abbreviations see Figure 7.

the triglyceride with the highest melting temperature in the PS/sesame oil system (28); however, once it crystallizes under isothermal conditions, it may promote the crystallization (e.g., heterogeneous crystallization) of other triglycerides with lower melting points (i.e., PPS_t, POST_t, and PPO). In blends of sesame oil with TP, values of n between 2 and 4 have been obtained (8). However, in that study pure TP was used. Additionally, the

crystallization process was followed through transmittance measurements, and crystal birefringence might have affected the transmittance values modifying the crystallization curve in comparison with the one obtained by DSC. In polymer crystallization, Avrami crystallization curves determined by DSC provide different information and n values than the ones obtained by transmitted polarized light microscopy (32). Since hetero-

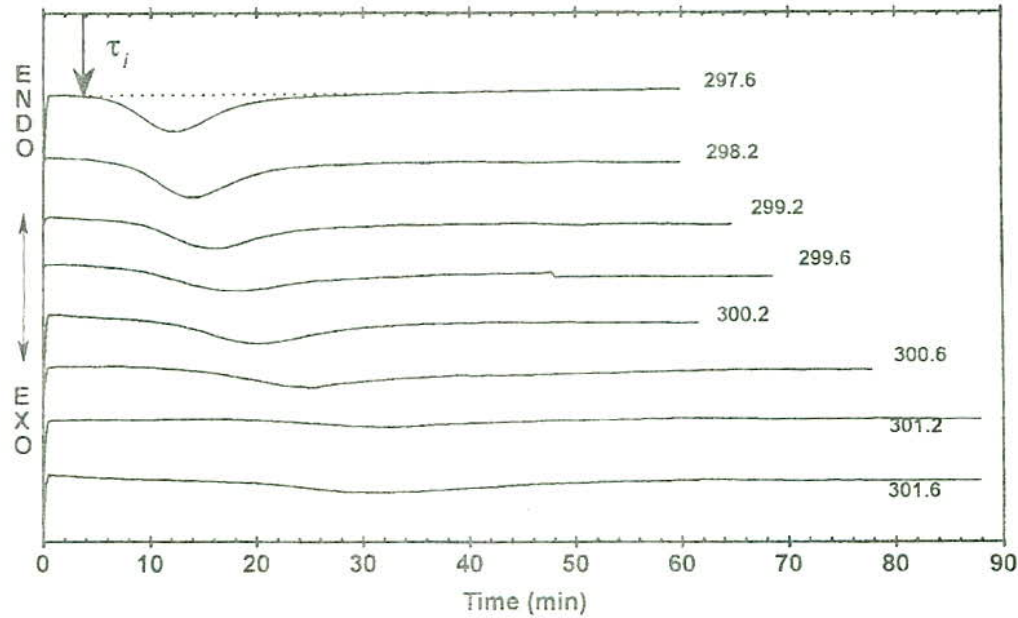


FIG. 10. DSC isothermal profile for the 26% PS in sesame oil at different temperatures. The induction time for crystallization (τ_i) is shown for a given temperature. For abbreviation, see Figure 2.

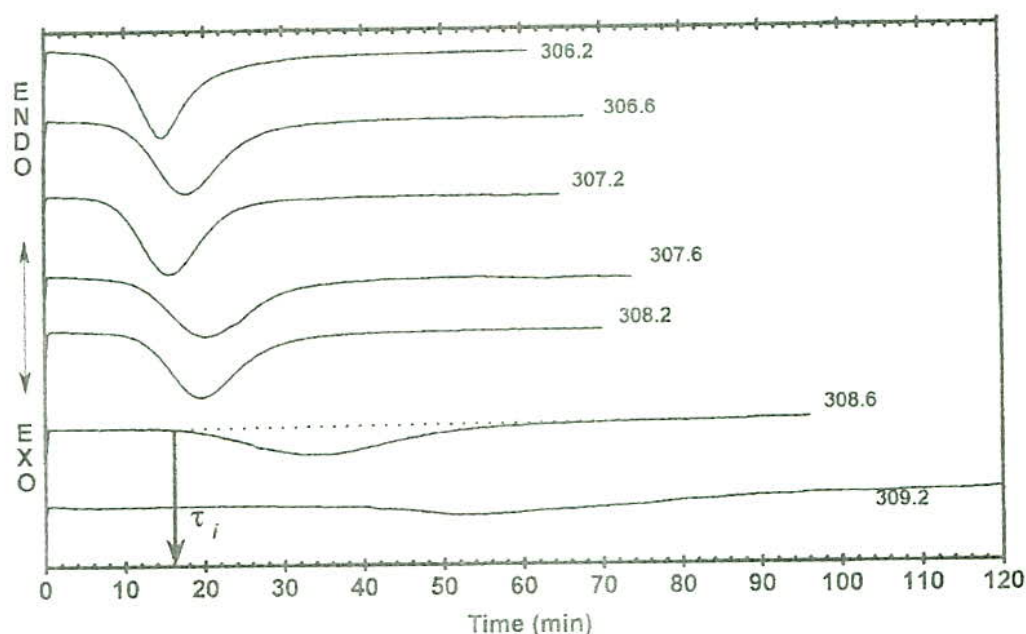


FIG. 11. DSC isothermal profile for the 80% PS in sesame oil at different temperatures. The induction time for crystallization (τ_i) is shown for a given temperature. For abbreviations see Figures 2 and 10.

geneous nucleation, sporadic nucleation, and secondary crystallization are more prevalent as crystallization time goes on, the intrinsic birefringence of crystals is not constant with time. This is evident from microphotographs in Figures 8 and 9. As a result, events like heterogenous nucleation and secondary crystallization might be more evident with the measurement of transmitted light than with DSC.

Figures 10 and 11 show the isothermal DSC profiles (i.e., isothermal crystallization) for the 26 and 80% PS/sesame oil solutions. In palm oil, two exotherms, I and II in order of generation, were obtained under isothermal conditions at temperatures lower than 297 K; at temperatures of 299 K or higher, peak I disappeared (19). In the present study only one exotherm of crystallization was obtained in all cases. The corresponding

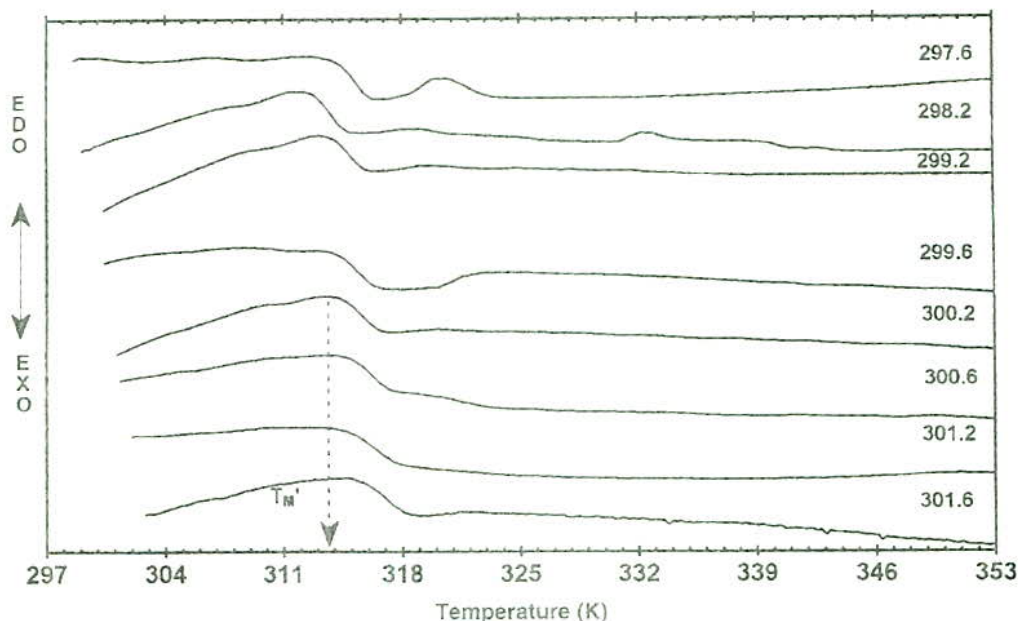


FIG. 12. Melting profile for crystals obtained in the 26% PS blend in sesame oil according to the conditions shown in Figure 7. For abbreviation see Figure 7.

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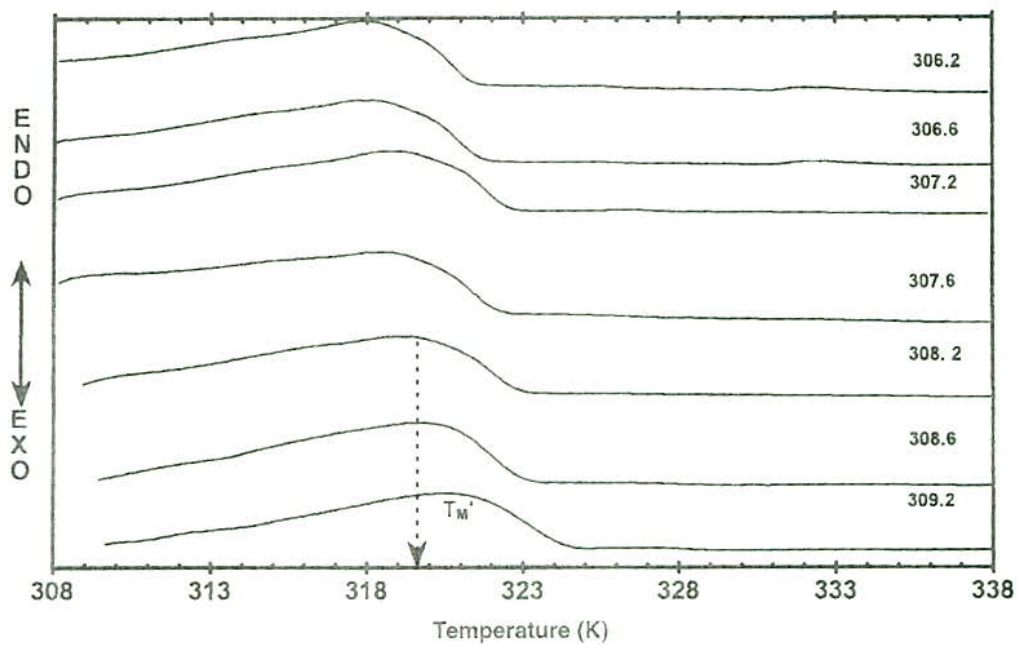


FIG. 13. Melting profile for crystals obtained in the 80% PS blend in sesame oil according to the conditions shown in Figure 8. For abbreviation see Figures 2 and 7.

melting profile of the crystals showed a major endothermic peak, with melting completed at temperatures lower than 320 K in the 26 (Fig. 12) and 42% blends (data not shown), and at temperatures lower than 324 K in the 60 (data not shown) and 80% blends (Fig. 13). The melting peak temperature associated with this endotherm was utilized as T_M' to establish the magni-

tude of τ_M^o (Figs. 12 and 13). Additional endothermic peaks of smaller size also were observed, which were related with melting events at higher temperatures. These peaks were more apparent at lower temperature of crystallization and thus were more apparent in the 26% PS/sesame oil solution than in the rest of the blends (Figs. 12 and 13). Based on the investigations

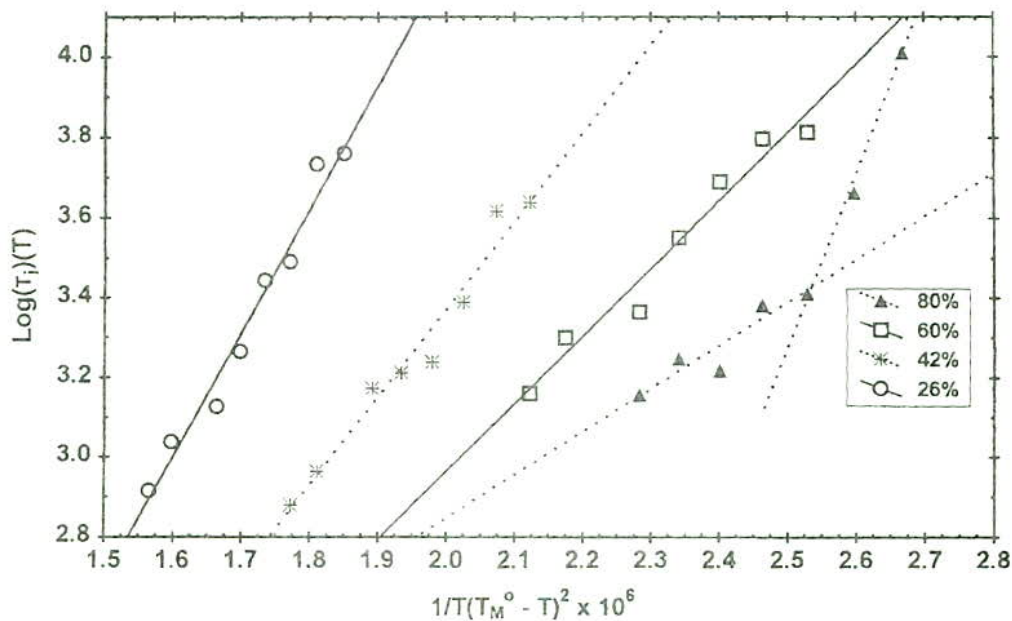


FIG. 14. Fitting of the nucleation kinetics of PS blends in sesame oil according to the Fisher-Turnbull equation. For abbreviations see Figures 2 and 7.

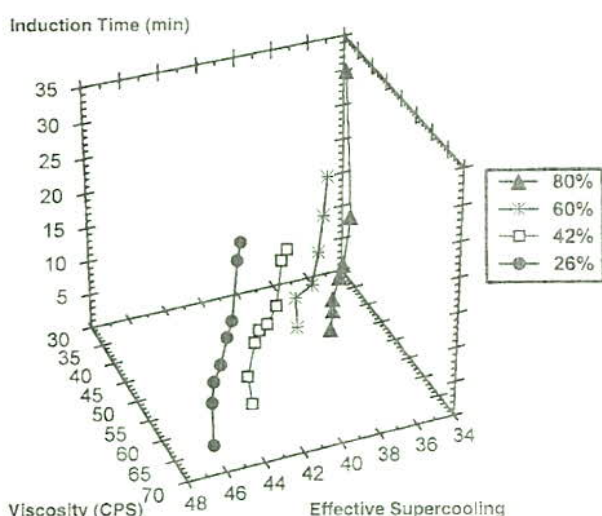


FIG. 15. Association among the induction time for crystallization, viscosity of the oil phase, and effective supercooling for the PS blends in sesame oil. See Figure 7 for abbreviation.

of Kawamura (19,33), the results indicate that the crystallization peak obtained in the 26, 42, and 60% PS/sesame oil solutions corresponded to β_1' crystals, probably mixed with α crystals. The proportion of α to β_1' depended on the temperature of crystallization; thus, the lower the crystallization temperature the more α crystals were present, decreasing the melting temperature of the major endothermic peak. On the other hand, the minor melting peaks observed in the heating thermograms of the crystals obtained at the lower crystallization temperatures (i.e., $T \leq 300.2$ K, Fig. 12) were associated with β_1 crystals. These crystals probably developed through a polymorph transformation from α crystals, the earlier transition to β_1' crystals occurring at the beginning of the isothermal crystallization (32). However, as the temperature of crystallization increased in the 26, 42, and 60% PS/sesame oil solution, β_1' crystallization predominated over α , and no $\alpha \rightarrow \beta_1' \rightarrow \beta_1$ transformation occurred (i.e., $T \geq 300.6$ K, Fig. 12). Since these minor peaks were derived from a polymorph transformation, they were not considered in the determination of T_M^o . The microphotographs shown in Figure 7 support these observations since at $T = 297.6$ K, the lower crystallization temperature utilized with the 26% PS/sesame oil solution, two different types of crystals developed (i.e., β_1' crystals mixed with α crystals) (Fig. 7A). When the crystallization temperature was increased to 299.2 K, just one type of crystal was developed (i.e., β_1' crystallization predominated over α) (Fig. 7B). In contrast, in the 80% PS/sesame oil solution, where in general higher crystallization temperatures were used (Fig. 11), the crystals obtained at $T \leq 307.6$ K were associated with the β_1' polymorph state (Fig. 8) while crystals developed at $T \geq 308.2$ K crystallized in the β_1 polymorph state (Fig. 9). The fitting of the nucleation kinetics of PS in sesame seed oil to the Fisher-Turnbull equation (Fig. 14) supported these observations. Thus, a good linearity was observed within the effective supercooling interval investigated

($r > 0.98$, $P < 0.0001$) for the 26, 42, and 60% PS/sesame oil solutions. However, with the 80% PS/sesame oil solution a discontinuity in the plot was evident around 307 K. This behavior showed that within the interval of effective supercooling investigated, the 26, 42, and 60% PS/sesame oil solutions crystallized mainly in a particular polymorph state (i.e., β_1' mixed with some α particularly at very low supercooling, Fig. 7A), while the 80% solution crystallized in two different polymorph states (i.e., β_1' at $T \leq 307.6$ K and β_1 at $T \geq 308.2$ K, Figs. 8 and 9).

The ΔG_c values for the PS/sesame oil solutions as a function of the crystallization temperature are shown in Table 2. Lower ΔG_c values have been obtained for palm oil, PS (21), and hydrogenated sunflower oil (22). In these studies a relative supercooling (i.e., $T_s - T$) rather than the effective supercooling (i.e., $T_M^o - T$) was utilized in the calculation of ΔG_c (Eqs. 4 and 5) since the value of T_M^o was not established. Formal studies that evaluate the effect of supercooling require the determination of T_M^o (23,34). From the results in Table 2, it is evident that as the temperature of crystallization increases and the PS is more diluted in sesame oil, PS crystallization is more difficult (i.e., ΔG_c increases). A particular case represented the β_1 crystallization (i.e., 80% PS at $T \geq 308.2$ K) since its ΔG_c values indicated a significantly more difficult nucleation than the β_1' polymorph. Our data showed that in spite of the higher concentrations of PS in the 80% PS/sesame oil system, crystallization in the β_1 state required more energy for its development than β_1' crystallization in the 26, 42, and 60% PS/sesame oil.

As we mentioned earlier, the rate of nucleation from the melt, J , depends on both ΔG_c and the activation free energy for molecular diffusion, ΔG_d . The viscosity is a physical parameter inversely proportional to molecular diffusion. Thus, the effect of the viscosity of the oil phase on τ_i , as a function of the effective supercooling is shown in Figure 15. Overall, the effective supercooling was higher for the 26 and 42% PS solutions and lower for the 60 and 80% PS solutions. For a particular PS solution the increment in the effective supercooling produced a higher viscosity of the oil phase and a decrease in the τ_i (Fig. 15). This behavior has the following explanation. Under the supercooling conditions investigated and at the low cooling rate used (i.e., 1 K/min), triglyceride molecules have enough time to organize in the liquid state in lamellar structures (see Ref. 9) while the temperature decreases. As a result, an increase in viscosity is observed. Thus, once isothermal conditions have been achieved, the lamellar structures of the triglycerides further organize and achieve a critical size to develop a stable nucleus. This last process will take place in shorter time (i.e., smaller τ_i) the longer the system takes to achieve isothermal conditions (i.e., the higher the effective supercooling). Further increments in the effective supercooling (e.g., lowering even more the crystallization temperature) resulted in crystallization even before achieving the corresponding isothermal temperature. Non-isothermal crystallization follows different kinetics (15) and was not evaluated in the present investigation.

It is generally accepted that molecular diffusion decreases with decreasing temperature. Thus, as effective supercooling increases, the crystal size resulting from crystallization must

decrease. In fact, this has been shown in TP crystallization in sesame oil using measurements of relative supercooling (i.e., $T_S - T$) and the crystallization rate constant (z , Eq. 2) (35). The β_1' (and α) crystals from PS, developed at the highest effective supercooling investigated (Fig. 7), were smaller than the β_1 crystals obtained in the 80% PS solution at the lower effective supercooling (Fig. 9). In general, β' form and small size confer a fine crystal network that incorporates large amounts of liquid oil and provides good spreadability and plasticity to margarines, shortenings, and vegetable spreads (29). In contrast, β form, larger size, and higher melting temperature than β' crystals provide a sensation of sandiness and a dull appearance to margarines and spreads (29).

From the above, the occurrence of a $\beta' \rightarrow \beta$ polymorphic transition is important to establish the functionality of PS in blends with sesame oil to produce value-added products like margarines and, overall, vegetable spreads. Gibon *et al.* (25) showed that the β' state of PPP is less prone to the $\beta' \rightarrow \beta$ polymorphic transition when crystallized directly from the melt (i.e., PS/sesame oil solution) than when occurring through the process $\alpha \rightarrow \beta' \rightarrow \beta$. According to the authors this phenomenon is due to a better "crystalline perfection" of the β' lattice obtained directly and slowly modified from the melt. The processing conditions to achieve a stable β' state must be established in the PS/sesame oil solutions to produce products acceptable to the consumers. One limiting aspect regarding the use of PS in blends with sesame oil is the consumer concern regarding the cholesterol-raising effect of saturated (i.e., palmitic acid) fatty acids. However, the positional distribution of palmitic acid in palm oil is predominantly in the *sn*-1 and *sn*-3 positions of the triglycerols, whereas in animal fats palmitic acid occupies mainly the *sn*-2 position. This difference in the positional distribution of palmitic acid in the triglycerols might account for the thrombogenic effect observed in animal fats which is not significantly present when palm oil or its derivatives are consumed by rats or humans (36,37).

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Review Article

Palm fruit chemistry and nutrition*

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The palm fruit (*Elaeis guineensis*) yields palm oil, a palmitic-oleic rich semi solid fat and the fat-soluble minor components, vitamin E (tocopherols, tocotrienols), carotenoids and phytosterols. A recent innovation has led to the recovery and concentration of water-soluble antioxidants from palm oil milling waste, characterized by its high content of phenolic acids and flavonoids. These natural ingredients pose both challenges and opportunities for the food and nutraceutical industries. Palm oil's rich content of saturated and monounsaturated fatty acids has actually been turned into an asset in view of current dietary recommendations aimed at zero trans content in solid fats such as margarine, shortenings and frying fats. Using palm oil in combination with other oils and fats facilitates the development of a new generation of fat products that can be tailored to meet most current dietary recommendations. The wide range of natural palm oil fractions, differing in their physico-chemical characteristics, the most notable of which is the carotenoid-rich red palm oil further assists this. Palm vitamin E (30% tocopherols, 70% tocotrienols) has been extensively researched for its nutritional and health properties, including antioxidant activities, cholesterol lowering, anti-cancer effects and protection against atherosclerosis. These are attributed largely to its tocotrienol content. A relatively new output from the oil palm fruit is the water-soluble phenolic-flavonoid-rich antioxidant complex. This has potent antioxidant properties coupled with beneficial effects against skin, breast and other cancers. Enabled by its water solubility, this is currently being tested for use as nutraceuticals and in cosmetics with potential benefits against skin aging. A further challenge would be to package all these palm ingredients into a single functional food for better nutrition and health.

Key words: palm oil, fatty acids, cardiovascular disease, cancer, vitamin E, carotenoids, flavonoids

Introduction

The oil palm is a monocotyledon belonging to the genus *Elaeis*. It is a perennial tree crop and the highest oil producing plant, yielding an average of 3.7 tonnes of oil per hectare per year in Malaysia. The crop is unique in that it produces two types of oil. The fleshy mesocarp produces palm oil, which is used mainly for its edible properties and the kernel produces palm kernel oil, which has wide application in the oleochemical industry. The genus *Elaeis* comprises two species, namely *E. guineensis* and *E. oleifera*. *E. guineensis* originates from West Africa and the commercial planting material is mainly of this species. *E. oleifera* is a stumpy plant of South American origin and its oil is characterised by a high oleic acid content. Currently, most of the world's production of palm oil comes from South-East Asia, in particular Malaysia and Indonesia. Malaysian crude palm oil production increased from 8.3 million tonnes in 1998 to 11.2 million tonnes in 2002, maintaining the country's position as the world's largest supplier of palm oil. Currently palm oil accounts for about 13% of the total world production of oils and fats and is expected to overtake soybean oil as the most important vegetable oil.

Origin

Elaeis guineensis originating from West Africa was first introduced to Brazil and other tropical countries in the

15th Century by the Portuguese.² However, its ropagation did not take off until the 19th Century when the Dutch brought seeds from West Africa to Indonesia resulting in four seedlings planted in Bogor, Indonesia in 1848. The palms were *dura* and the progenies from these seedlings were planted as ornamentals in Deli and became known as Deli *Dura*. From there the oil palm was sent to the Botanical Gardens in Singapore in 1875, and subsequently brought to Malaya (as West Malaysia was then known) in 1878. The oil palm was initially planted in Malaya as an ornamental and the first commercial planting was only in 1917.

Elaeis oleifera from South America has higher oleic and linoleic acid content and lower content of palmitic and other saturated acids. The iodine value ranges from 78-80. The current main interest in *E. oleifera* is in the potential of transmitting its useful characters to inter-specific hybrids with *E. guineensis*. The oil palm fruit is a drupe, which forms in a tight bunch.

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The pericarp comprises three layers: the exocarp (skin); mesocarp (outer pulp containing palm oil); and endocarp (a hard shell enclosing the kernel (the endosperm) which contains oil and carbohydrate reserves for the embryo). Fruit development starts at approximately two weeks after anthesis (WAA). Oil deposition in the endosperm starts at approximately 12 WAA and is almost complete by 16 WAA.³ During this period the endosperm and endocarp slowly harden and by 16 WAA the endocarp is a hard shell enclosing a hard white endosperm – the kernel. Oil deposition in the mesocarp starts at approximately 15 WAA and continues until fruit maturity at about 20 WAA. The fruits on a bunch do not ripen simultaneously owing to slight variation in the time of pollination. Fruits at the end of each spikelet ripen first and those at the base last. Fruits on the outside of the bunch are large and deep orange when ripe while the inner fruits are smaller and paler.

In the commercial Malaysian tenera variety, the neutral lipids, especially triacylglycerols (TG), increase rapidly from 16 WAA onwards, along with the parallel accumulation of total lipids, reaching their maximum at 20 WAA. The polar lipids simultaneously decrease to less than 1% of the total lipids at 20 WAA. The Nigerian dura variety follows a similar pattern except that rapid TG accumulation occurs between 18-22 WAA. Palmitoleic and linolenic acids are present in significant amounts in the early stages of lipid synthesis. These are typical chloroplast and membrane fatty acids, reflecting a high ratio of chloroplast and cellular synthesis to storage lipid synthesis. These fatty acids however are undetectable after 16 WAA, probably greatly diluted by the accumulation of storage lipids. The immature mesocarp contains large amounts of chlorophyll which decline by about 17 WAA, accompanied by a massive accumulation of carotenes as the fruit ripens.⁴ Also characteristic of the immature green mesocarp are large amounts of sterols. As the fruit matures, the sterols decrease as a consequence of dilution by the tremendous amount of TG synthesised.

Chemistry of palm oil

Like all oils, TGs are the major constituents of palm oil. Over 95% of palm oil consists of mixtures of TGs, that is, glycerol molecules, each esterified with three fatty acids. During oil extraction from the mesocarp, the hydrophobic TGs attract other fat- or oil-soluble cellular components. These are the minor components of palm oil such as phosphatides, sterols, pigments, tocopherols, tocotrienols and trace metals. Other components in palm oil are the metabolites in the biosynthesis of TGs and products from lipolytic activity. These include the monoacylglycerols (MGs), diacylglycerols (DGs) and free fatty acids (FFAs).

The fatty acids belong to the class of aliphatic acids, such as palmitic (16:0), stearic (18:0) and oleic (18:1) in animal and vegetable fats and oils. The major fatty acids in palm oil are myristic (14:0), palmitic (16:0), stearic (18:0), oleic (18:1) and linoleic (18:2).⁵ The typical fatty acid composition of palm oil from Malaysia is presented in Table 1. Palm oil has saturated and unsaturated fatty acids in approximately equal amounts. Most of the fatty acids are present as TGs. The different placement of fatty

Table 1. Typical fatty acid composition (%) of palm oil

Fatty acid chain length	Mean	Range observed	Standard deviation
12:0	0.3	0 - 1	0.12
14:0	1.1	0.9 - 1.5	0.08
16:0	43.5	39.2 - 45.8	0.95
16:1	0.2	0 - 0.4	0.05
18:0	4.3	3.7 - 5.1	0.18
18:1 (n-9)	39.8	37.4 - 44.1	0.94
18:2 (n-6)	10.2	8.7 - 12.5	0.56
18:3	0.3	0 - 0.6	0.07
20:0	0.2	0 - 0.4	0.16

Table 2. Triacylglycerol composition (%) of Malaysian tenera palm oil

No Double Bond		1 Double Bond		2 Double Bonds		3 Double Bonds		≥4 Double Bonds	
MPP	0.29	MOP	0.83	MLP	0.26	MLO	0.14	PLL	1.08
PMP	0.22	MPO	0.15	MOO	0.43	PLO	6.59	OLO	1.71
PPP	6.91	POP	20.02	PLP	6.36	POL	3.39	OOL	1.76
PPS	1.21	POS	3.50	PLS	1.11	SLO	0.60	OLL	0.56
PSP	0.12	PMO	0.22	PPL	1.17	SOL	0.30	LOL	0.14
	-	PPO	7.16	OSL	0.11	OOO	5.38		
		PSO	0.68	SPL	0.10	OPL	0.61		
		SOS	0.15	POO	20.54	MOL	-		
		SPO	0.63	SOO	1.81				
				OPO	1.86				
				OSO	0.18				
				PSL	-				
Others	0.16		0.34		0.19		0.15		0.22
Total	9.57		33.68		34.12		17.16		5.47

Kifli (1981)⁶ M, myristic; P, palmitic; S, stearic; O, oleic; L, linoleic

acid types on the glycerol molecule produces a number of different TGs. There are 7% to 10% of saturated TGs, predominantly tripalmitin.⁶ The fully unsaturated TGs constitute 6 to 12%. The Sn-2 position has specificity for unsaturated fatty acids. Therefore, more than 85% of the unsaturated fatty acids are located in the Sn-2 position of the glycerol molecule. Table 2 shows the percentage distribution of individual TGs of palm oil. The triacylglycerols in palm oil partially define most of the physical characteristics of the palm oil such as melting point and crystallisation behaviour.

Minor constituents of palm oil

The minor constituents can be divided into two groups. The first group consists of fatty acid derivatives, such as partial glycerides (MGs, DGs), phosphatides, esters and sterols. The second group includes classes of compounds not related chemically to fatty acids. These are the hydrocarbons, aliphatic alcohols, free sterols, tocopherols, pigments and trace metals.⁷

Most of the minor components found in the unsaponifiable fraction of palm oil are sterols, higher aliphatic alcohols, pigments and hydrocarbons. The other minor components, such as partial glycerides and phosphatides, are saponifiable by alkaline hydroxide. The partial glycerides do not occur naturally in significant amounts except in palm oil from damaged fruits. Such oils would have undergone partial hydrolysis resulting in the production of free fatty acids, water and the partial glycerides. Different isomers of MGs and DGs are found in palm oil. α -MGs are more stable than their β -isomers. As in most vegetable oils, the α,α' -DGs (or 1,3 DGs) are the predominant DGs in palm oil.

Several minor nonglyceride compounds are found in palm oil. Table 3 gives the levels of these minor components in the oil. The nonglyceride fraction of palm oil

Table 3. Ranges in content for various components in the unsaponifiable fraction from a palm oil

Component	%	Mg/kg (in palm oil)
Carotenoids		
α -carotene	36.2	
β -carotene	54.4	
γ -carotene	3.3	500 - 700
Lycopene	3.8	
Xanthophylls	2.2	
Vitamin E		
α -tocopherol	28	
α -tocotrienol	29	500 - 800
γ -tocotrienol	28	
δ -tocotrienol	14	
Sterols		
Cholesterol	4	
Campesterol	21	~300
Stigmasterols	21	
β -sitosterol	63	
Phosphatides		500 - 1000
Total alcohols		
Triterpenic alcohol	80	
Aliphatic alcohol	20	~800

consists of sterols, triterpene alcohols, tocopherols, phospholipids, chlorophylls, carotenoids and volatile flavour components, such as aldehydes and ketones. Sterols are tetracyclic compounds with generally 27, 28 or 29 carbon atoms. They make up a sizeable portion of the unsaponifiable matter in oil. The content of sterols in palm oil is about 0.03% of its total composition. Cholesterol (2.2-6.7%), Δ^5 -avenasterol (0-2.8%) Δ^7 -stigmasterol (0-2.8%) and Δ^7 -avenasterol (0-4%) was also found in the sterol fraction (326-627 mg/kg) of palm oil.⁷ Most of the sterols are relatively inert and do not appear to contribute to any important property to palm oil. However, Δ^5 -avenasterol has been reported to show antioxidant activity in edible oils.

Tocopherols and tocotrienols are fat-soluble vitamin E isomers and the major antioxidants of vegetable oils. Tocopherols can be divided into two families, namely tocopherols and tocotrienols. In tocopherols, the side chain is saturated while in tocotrienols it is unsaturated. Tocotrienols are rarely seen in vegetable oils with the exception of palm and rice bran oils. Crude palm oil contains 600 to 1000 ppm of tocopherols and tocotrienols. Refining reduces the level down to 350-630 ppm (Table 4). Both tocopherols and tocotrienols are composed of four different isomers, referred to as α , β , γ or δ , depending upon the number and position of methyl groups attached to the chromane rings. The major vitamin E isomers in palm oil are α -tocotrienol (29%), α -tocopherol (28%) and δ -tocotrienol (14%).⁸ Besides playing a beneficial biological role as radical quenchers in vivo, tocopherols and tocotrienols are also antioxidants, which contribute to the stability of palm oil. Tocopherols can interrupt lipid oxidation by inhibiting hydroperoxide formation in the chain-propagation step, or the decomposition process by inhibiting aldehyde formation. Besides its free radical scavenging activity, α -tocopherol is highly reactive towards singlet oxygen and protects the oil against photosensitised oxidation.

The pigmentation of palm fruits is related to their stage of maturity. Two classes of natural pigments occurring in crude palm oil are the carotenoids and the chlorophylls. Palm oil from young fruits contains more chlorophyll and less carotenoids than oil from mature or ripe fruits. The pigments in palm oil are involved in the mechanisms of autooxidation, photooxidation and antioxidant within the plant.⁹ Carotenoids are highly unsaturated tetraterpenes bio-synthesized from eight isoprene units. Their more favoured state is the all-*trans*. Carotenoids are divided into two main classes: carotenes, which are strictly polyene hydrocarbons, and xanthophylls, which contain oxygen. The oxygen in xanthophylls may be in the form of hydroxy (e.g. zeaxanthin and lutein), keto, epoxy or carboxyl groups. The simplest carotene is lycopene.

Crude palm oil has a rich orange-red colour due its high content of carotene (700-800 ppm). The major carotenoids in palm oil are β - and α -carotene, which account for 90% of the total carotenoids.¹⁰ There are about 11 different carotenoids in crude palm oil. The major types and composition of carotenoids (Table 5) extracted from oils of different palm species were studied by Yap *et al.*¹⁰

Table 4. Tocopherol and tocotrienol content (mg/kg) of common refined edible oils

Tocol Isomers	Soybean oil	Corn oil	Olive oil	Sunflower oil	Milk fat (ghee)	Wheat germ oil	Rice bran oil	Palm oil	Palm olein	Palm stearin
α-Tocopherol	117.2	248.9	151.4	485.2	32.7	218.9	64	188.2	179.0	50.0
β-Tocopherol	19.8	10.1	13.3	3.0	n.d.	33.2	10.6	n.d.	n.d.	n.d.
γ-Tocopherol	560.7	464.1	10.9	51.0	n.d.	84.7	n.d.	n.d.	17.6	n.d.
δ-Tocopherol	178.2	58.2	n.d.	n.d.	33.8	n.d.	187	n.d.	n.d.	n.d.
α-Tocotrienol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	31.4	198.1	219.9	47.4
β-Tocotrienol	20.2	n.d.	n.d.	n.d.	n.d.	347.5	83.2	10.0	8.1	9.0
γ-Tocotrienol	6.2	n.d.	n.d.	8.3	n.d.	n.d.	783.2	198.8	332.7	134.9
δ-Tocotrienol	n.d.	n.d.	n.d.	n.d.	n.d.	18.4	38.6	98.4	67.0	31.4
Total	902.2	781.4	175.6	547.5	66.5	702.7	1198	693.5	824.3	272.8

Sundram & Nor⁸

Table 5. Carotene profiles of palm oil extracted from *Elaeis guineensis*, *Elaeis Oleifera* and their hybrids

	Carotene composition (%)						
	M	P	D	MP	MD	MD x P	T
Phytoene	1.12	1.68	2.49	1.83	2.45	1.30	1.27
Cis-β-carotene	0.48	0.10	0.15	0.38	0.55	0.42	0.68
Phytoene	Trace	0.90	1.24	Trace	0.15	Trace	0.06
β-carotene	54.08	54.39	56.02	60.53	56.42	51.64	56.02
α-carotene	40.38	33.11	54.35	32.70	36.40	36.50	35.16
Cis-α-carotene	2.30	1.64	0.86	1.37	1.38	2.29	2.49
ζ-carotene	0.36	1.12	2.31	1.13	0.70	0.36	0.69
γ-carotene	0.09	0.48	1.10	0.23	0.26	0.19	0.33
δ-carotene	0.09	0.27	2.00	0.24	0.22	0.14	0.83
Neurosporene	0.04	0.63	0.77	0.23	0.08	0.08	0.29
β-zeacarotene	0.57	0.97	0.56	1.03	0.96	1.53	0.74
α-zeacarotene	0.43	0.21	0.30	0.35	0.40	0.52	0.23
Lycopene	0.07	4.50	7.81	0.05	0.04	0.02	1.30
Total carotene (ppm)	4592	428	997	1430	2324	896	673

Yap *et al.*¹⁰ in *M = *E. oleifera* (Melanococca), P = *E. guineensis* (pisifera), D = *E. guineensis* (dura); *T = *E. guineensis* (tenera)

They found 13 different types of carotenoids with the major isomers, α-carotene and β-carotene, accounting for 54% to 60% and 24% to 60% of the total carotenoids, respectively. No significant difference in the types of carotenoids was found in the oils of *E. oleifera* and *E. guineensis*, and their hybrids and backcrosses to *E. guineensis*. The study also showed that *E. guineensis* contained a higher level of lycopene compared to *E. oleifera* and its hybrids with *E. guineensis*.

Carotenoids are the precursors of vitamin A, with β-carotene having the highest provitamin A activity. Palm oil has 15 times more Retinol Equivalents than carrot and 300 times more than tomato. Carotenes are sensitive to oxygen and light. The oxidation of carotenes is accelerated by hydroperoxides generated from lipid oxidation, leading to discolouration and bleaching α- and β-

ionones, β-13 and β-14-apocarotenals and β-13-apocrotenone are among the carotenoids.

In refining crude palm oil, the carotenoids are first partially removed by adsorption on an activated earth following which high temperature steam deodorization destroys the chromogenic properties of the remaining carotenoids to produce a light yellow refined palm oil. With carotene as a rich source of vitamin A, a process was developed by Choo and co-researchers¹¹ to produce a deacidified and deodorised red palm oil which retains as much as 80% of the original carotenoids. A red palm oil produced from this process, bearing the trade name 'CAROTINO', is available in the market.

The fatty acid composition of palm oil (≈1:1 saturated to unsaturated fatty acids) is such that the oil is semi-solid at normal room temperature. This property and the oil

melting range permit its use as a major component in margarine and shortening without hydrogenation.¹² Thus, for most practical purposes, palm oil does not need hydrogenation. Nonetheless, the use of this process has been explored to maximise the utilisation of palm oil and its fractions in edible food products. Palm stearin is an excellent and economic starting material for certain food and non-food applications where fully hydrogenated fats are required. Cake shortenings made from palm oil products such as hydrogenated or interesterified palm oil, in combination with butterfat, produce cakes with better baking properties than cakes made with 100% butterfat. Whereas the butterfat gave the cakes the desired buttery flavour, the palm products enhanced the baking performance. Some hydrogenated products of palm oil and its products are also suitable for application in a number of high premium speciality products, such as toffee and confectionery fats.

Apart from palm oil and the fat-soluble minor constituents described above, the palm fruit contains large amounts of water-soluble phenolic compounds and flavonoids. These are basically extracted into the steriliser condensate and the palm oil milling effluent (POME) during the milling process. The sterilisation of palm fruits inactivates polyphenoloxidases and retains the phenolics and flavonoids. These are water soluble and demonstrated to have potent antioxidant properties.¹³ A recent technology developed at the Malaysian Palm Oil Board (MPOB) uses an ecologically friendly process in which the constituent water added during the sterilisation of palm fruits is used to retain the compounds of interest for passage through a series of innovative separation techniques that isolate specific compounds of interest on the basis of their molecular weights. The final aqueous product can be further processed depending upon its intended applications.

Nutritional properties of palm oil and its components

Almost 90% of the world palm oil production is used as food. This has made demands that the nutritional properties of palm oil and its fractions be adequately demonstrated. The fatty acid composition of palm oil has thus been the focus of attention in determining its nutritional adequacy in relation to coronary heart disease (CHD) risk factors. As mentioned earlier, palmitic acid (44%) is the major saturated fatty acid in palm oil and this is balanced by almost 39% monounsaturated oleic acid and 11% polyunsaturated linoleic acid. The remainder is largely stearic (5%) and myristic (1%) acids. This composition is significantly different from palm kernel oil (obtained as a co-product during the processing of oil palm fruits) which is almost 85% saturated. The results of a large number of dietary trials in animals and humans have been published and reviewed previously.⁷ These studies have yielded results that not only demonstrate the nutritional adequacy of palm oil and its products, but have also caused transitions in the understanding of the nutritional and physiological effects of palm oil, its fatty acids and minor components.

The minor components of interest in palm oil are the vitamin E, carotenoids and an antioxidant-rich phenolic-flavonoid complex recovered from the palm oil milling

waste. The technology to isolate and concentrate these components has led to their use in several studies aimed at understanding their physiological effects. Accordingly, the emphasis has been on the cholesterol lowering effects of palm oil tocotrienols, the pro-vitamin A activity of red palm oil and palm carotene concentrates and the antioxidant and anti-cancer properties of palm vitamin E, carotenoids and the phenolic-flavonoid complex. These findings currently supported by a large volume of scientific publications, which are discussed briefly.

Human Studies

Effects of palm oil/olein as part of a low-fat healthy diet

Palm oil when consumed as part of a low-fat diet (<30% energy) has been shown to be effective in maintaining desirable plasma cholesterol and lipoprotein cholesterol levels.¹⁴ Monounsaturated oils rich in oleic acid are currently touted to be the healthiest of the edible fats in the human diet. While olive, rapeseed and canola have in excess of 60% of their fatty acid composition as cis-oleic acid, palm olein has about 48% of this monounsaturated fatty acid. The question of whether this level of oleic acid in palm olein is adequate to result in a lipoprotein-cholesterol profile that protects against coronary heart disease (CHD) was examined in a series of human trials. In these studies the exchange between palm olein (rich in 16:0) and olive oil (rich in 18:1) resulted in similar plasma and lipoprotein cholesterol values (total cholesterol, TC, low-density lipoprotein cholesterol, LDL-C and high density lipoprotein cholesterol, HDL-C). This showed that in healthy normocholesterolaemic humans, palm olein could be exchanged for olive, canola and rapeseed oils (high oleic) without adversely affecting serum lipids and lipoprotein levels.¹⁴

Sundram *et al.*,¹⁵ fed 23 healthy normocholesterolaemic male volunteers carefully designed whole food diets containing canola oil (18:1-rich), palm olein (16:0-rich) or an American Heart Association Step 1 diet (AHA), all contributing approximately 31% energy as fat and <200mg dietary cholesterol/day. The AHA oil blend was obtained by blending soyabean oil (50%), palm oil (40%) and canola oil (10%) which resulted in a 1:1:1 ratio of the saturates, monounsaturates and polyunsaturates. Serum TC and LDL-C were not significantly affected by these three diets despite manipulations of the key fatty acids. The high 18:1 canola and high 16:0 palm olein resulted in almost identical plasma and lipoprotein cholesterol. Only HDL-C after the AHA diet was significantly raised compared with the other two diets. The findings of the above study have now become the subject of a patent¹⁶ advocating a balanced fatty acid ratio for maintaining a proper LDL/HDL-cholesterol ratio that could be cardio-protective.

When the habitual Dutch diet, which is characteristic of a typical Western diet, was maximally replaced with palm oil (~80% replacement) TC and LDL-C was unaffected. The palm oil diet however resulted in significant improvements in the HDL2-C and the apolipoprotein A1/B ratio signalling some cardiovascular benefits rather than the converse.¹⁷ The above-mentioned studies focussed on the oleic acid content in the different oils tested (palm olein, canola, rapeseed and olive) for

their cholesterol modulating properties. Undoubtedly, oleic acid has been proven to have cholesterol-lowering properties, which are said to equal or better the poly-unsaturates. However, the optimum amount of oleic acid required to produce beneficial lipoprotein profiles has yet to be defined. In this context, palm olein containing 44%-48% oleic acid was similar in its plasma cholesterol and lipoprotein modulating effect to those of higher oleic acid containing oils including olive (70%), canola (65%) and rapeseed (60%). This augurs well for palm olein and its apparent lack of cholesterolaemic effects.

Effects of palm oil/olein in comparison to saturated fats

The human diet contains a mixture of fats, and, therefore, mixtures of fatty acids. The net effect of such a mixture on TC, individual lipoproteins or both will be the sum effects of all the fatty acids, some acting in opposite directions to each other. It is therefore important to decipher the key cholesterol modulating fatty acids to determine the cholesterolaemic index of the fat or oil consumed. Fortunately, several recent human studies have focused on these issues and have provided additional observations that tend to support the Hegsted¹⁸ observation that saturated fatty acids differ in their cholesterol regulating ability. Some of these studies that used palm oil as a source of 16:0 in their test diets demonstrated that the cholesterolaemic effect due to 16:0 (palmitic acid) is significantly lower than that of a lauric+myristic (LM, 12:0+14:0) combination. Coconut oil is almost 85% saturated and it has been suggested that the higher cholesterol values after a coconut oil diet may be simply due to the lower availability of linoleic acid. This suggestion has been discounted in the recent study of Sundram *et al.*¹⁹ Despite the incorporation of a high level of 18:2 (5.6% energy) into the LM diet, it induced significantly higher concentrations of TC and LDL-C in healthy volunteers compared to a 16:0-rich palm olein diet (3.3% energy as 18:2).

From the studies cited above we can see that the effect of palmitic acid (the major saturated fatty acid in palm oil products), on plasma lipoprotein cholesterol is becoming better understood. Indeed, if palmitic acid is hypercholesterolaemic, then an increased endogenous synthesis or a decreased clearance rate of cholesterol should be evident. The human study of French *et al.*,²⁰ investigated the relationship between endogenous synthesis of cholesterol and the content of palmitic acid in the diet contributed by palm oil. High levels of palmitic acid in the diet did not significantly affect serum total and LDL-cholesterol levels. Fractional synthesis rate of cholesterol was not different between dietary treatments (high versus low palmitic acid content). This suggested that there was no relation between endogenous synthesis of cholesterol and palmitic acid content in the diet.

Effects of palm oil/olein in comparison to trans fatty acids

Trans fatty acids negatively impact human plasma lipoprotein profile and have untoward implications for atherogenesis. Trans fatty acids deleteriously affect lipoproteins by increasing TC, LDL-C, lipoprotein Lp(a) and decreasing HDL-C relative to their cis isomers.²¹ This

has raised the need to replace hydrogenated fats with natural solid fats in a large number of food formulations. The nutritional efficacy of the solid fats replacing hydrogenated fats should be such that they do not adversely affect plasma lipids and other CHD risk factors. In this context, palm oil can be considered a suitable alternative. In several studies the impact of trans elaidic acid on the lipoprotein profile of humans appeared to be worse than that of saturates occurring in natural oils and fats.²² The solid fat profile of palm oil makes it a natural contender to replace hydrogenated fats in solid-fat food formulations. The use of palm oil in such products could virtually eliminate their trans fatty acid content. The desired fatty acid composition in the product can be easily achieved by blending palm and other oils. For example, this has been demonstrated previously in the AHA-blend,^{15,16} in which palm olein contributed 40% of the blend's composition and this resulted in an optimum LDL/HDL-cholesterol ratio.

Minor components in palm oil and their health effects

Some of the minor components in palm oil include the carotenoids, tocopherols, tocotrienols, sterols, phosphatides, triterpenic and aliphatic alcohols. Although these minor components account for less than 1% of the oil's constituents, they nevertheless play significant roles in maintaining its stability and quality. In addition, some of these minor components especially the carotenoids and vitamin E (tocopherols and tocotrienols) are of nutritional importance.

Palm vitamin E

Refined palm oil contains about 350-450ppm vitamin E, present as the RRR- α -tocopherol (30%) and tocotrienol (70%) isomers. In contrast, other oils such as corn, soya and sunflower are good sources of the tocopherols but contain no tocotrienols. Historically, vitamin E activity (one international unit, IU) has been defined as 1mg of all rac- α -tocopheryl acetate whereas 1mg of RRR- α -tocopherol equalled 1.49 IU. In addition, vitamin E activity in foods is expressed as the α -tocopherol equivalent (α -TE), which is the activity of 1mg of RRR- α -tocopherol.²³ On this basis, conversion factors for of each mg of the different tocopherols and tocotrienols present in palm oil to α -TE are as follows: α -tocopherol, 1.0; tocopherol, 0.5; tocopherol, 0.1; α -tocotrienol, 0.3 and β -tocotrienol, 0.05. The factors for gamma and delta tocotrienols are presently unknown. These conversion factors are based on the ability of each isomer to overcome specific vitamin E deficiency symptoms such as fetal resorption, muscular dystrophy and encephalomalacia. Since these factors are based on rat fetal resorption assays,²⁴ their relevance to humans is often questionable. In addition, their biological activity may be based on their antioxidant activities, but this too appears misleading. For example, α -tocotrienol has only one third the biological activity of α -tocopherol, yet it has a higher or equivalent antioxidant activity.⁷

There is now a growing interest in the nutritional and physiological properties of vitamin E in palm oil, especially those of the tocotrienols. This has recently been reviewed.^{25,26} Tocotrienols have attracted great interest

for their suggested ability to regulated plasma cholesterol levels by the inhibition of HMG-CoA reductase (HMGR) activity, which regulates cholesterol synthesis in the liver. The current data is however conflicting with respect to the ability of tocotrienols from different sources to beneficially lower plasma cholesterol in humans. Palm tocotrienols (TRF) may have potential anti-cancer properties. Sundram *et al.*,²⁷ suggested that crude palm oil was more effective than refined palm oil in increasing the tumour latency period in DMBA treated rats. This was attributed to the presence of tocotrienols and carotenoids in the crude oil. When the vitamin E content in palm oil was removed, significantly more tumours became apparent.²⁸ Addition of palm vitamin E to corn oil (500 or 1000ppm) resulted in a lower tumour incidence and occurrence compared to rats fed corn oil alone.

A series of studies also investigated the *in vitro* effects of tocotrienols on human breast cancer cells. Compared to α -tocopherol (500ug/ml concentration), which had no growth inhibition of human breast cancer cells, palm TRF inhibited the incorporation of (3H) thymidine into human breast cancer cells by 50% (at a concentration of 180ug/ml).²⁹ Osterogen-receptor negative and positive human breast cancer cells were used to test the efficacy of individual palm tocotrienols at varying concentrations. These individual tocotrienols showed even greater inhibitory effects on these cells and at much lower concentrations than TRF. There also appears to be a synergy in the inhibition of human cancer cells between palm tocotrienols and flavonoids. Combinations of tocotrienols, flavonoids and tamoxifen proved to be even more effective than the individual components.³⁰ Palm tocotrienols have also been reported to be effective against transplantable mice tumours.

Palm carotenoids

The mesocarp of the oil palm fruit yields a deep red coloured palm oil, which contains 700-800ppm carotenoids. The characteristics of these palm carotenoids and technological advances aimed at producing red palm oil and palm carotene concentrate have been discussed earlier. The provitamin A activity of carotenoids has been known for a long time. Only a few carotenoids are provitamins, and those that are, vary in their bio-availability. β -carotene is the most important vitamin A precursor in human nutrition and provides the major source of vitamin A in many developing countries.

β -carotene-rich red palm oil has been used in dietary intervention studies to evaluate its possible role in the prevention of vitamin A deficiency among populations at risk. In India, children 5-10 years old with keratomalacia were treated twice a day with an emulsion prepared with red palm oil. Each dose contained 0.6ml of red palm oil and therapy was continued for 15 days. The red palm oil treatment compared well with the results obtained by treating another group of keratomalacia patients with cod liver oil containing a similar dose of vitamin A.

Red palm oil is the richest natural source of β -carotene, a precursor of vitamin A, in addition to providing energy density to the diet. Rao³¹ summarised some aspects of the health and nutritional effects of red palm oil and the results of a comprehensive safety

evaluation carried out by the Indian Council for Medical Research at the National Institute of Nutrition. The purpose of this work was to recommend use of the oil in supplementary feeding programmes. Based on the results obtained, it was recommended that developing countries should have no hesitation in creating strategies to increase the use of red palm oil in combating vitamin A deficiency. The importance of red palm oil in the treatment of vitamin A deficiency has been reiterated by many others.³² These are easy to produce, available all year round, inexpensive and accessible sources of vitamin A for most of the developing world.

It was also observed that red palm oil could be blended with different edible oils without modifying the original taste of the oil, but with some slight colour change. The League of Nations Intergovernmental Conference on Rural Hygiene in the late 1930s recognized and recommended the possibility of making use of red palm oil as a source of provitamin A in malnourished populations. The XVIIth meeting of the International Vitamin A Consultative Group in Guatemala,³³ recommended among other measures, the use of red palm oil because its carotenoid content seems to be particularly bioavailable. Similar recommendations have also been made in a United Nations report.³⁴ Dietary intervention with red palm oil thus offers a good degree of protection from severe vitamin A deficiency.

Palm carotenoids and cancer prophylaxis

Doll and Peto³⁵ identified diet as one of the major factors in the aetiology of cancer. Cancer epidemiological studies have provided evidence that cancer chemopreventive agents exist naturally in our diets. High intakes of vegetables and fruits are known to be associated with lower risk of cancer of the lung and gastrointestinal tract. The protective effect may relate to different components present in fruits and vegetables. Although, over one thousand compounds have been tested, the retinoids and carotenoids have received the most attention. A number of epidemiological studies have demonstrated an inverse correlation between dietary intake or blood level of vitamin A/ carotenoids and cancer risk, as well as an anti-carcinogenic effect for these compounds. The data further indicate that a wide range of cancer sites may be influenced by these carotenoids.

The inhibition of chemical carcinogenesis by palm oil carotenoids with reference to Benzo(a) pyrene metabolites *in vivo* and *in vitro* in rat hepatic cells has been reported by Tan and Chu.³⁶ It has also been reported that palm carotenoids exhibit an inhibitory effect on the proliferation of a number of human cancer cells. These include the neuroblastoma, GOTO, pancreatic cancer PANC-1, glioblastoma A172 and gastric cancer HGC-27.³⁷ Of significant interest from these studies was the observation that palm α -carotene and a palm carotene concentrate were protective whereas synthetic β -carotene was tumour promoting. Murakoshi *et al.*,³⁸ isolated palm α -carotene and a palm carotene concentrate and showed its ability to inhibit liver, lung and skin tumours in mice. The same effect could not however be attributed to synthetic β -carotene. Similar superior inhibitory effects for α -carotene were

apparent in a chemically induced skin tumour progression model. Overall, these results lead to the conclusion that the natural bouquet of carotenoids, in palm oil has promising chemopreventive activities against cancer.

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DSC Study on the Melting Properties of Palm Oil, Sunflower Oil, and Palm Kernel Olein Blends Before and After Chemical Interesterification

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ABSTRACT: Changes in DSC melting properties of palm oil (PO), sunflower oil (SFO), palm kernel olein (PKOo), and their blends in various ratios were studied by using a combination of blending and chemical interesterification (CIE) techniques and determining total melting (ΔH_f) and partial melting (ΔH_{pc}) enthalpies. Blending and CIE significantly modified the DSC melting properties of the PO/SFO/PKOo blends. PO and blends containing substantial amounts of PO and PKOo experienced an increase in their DSC ΔH_f and ΔH_{pc} following CIE. The DSC ΔH_f and ΔH_{pc} of PKOo, blends of PO/SFO at 1:1 and 1:3 ratios, and all blends of PKOo/SFO significantly decreased after CIE. The DSC ΔH_f and ΔH_{pc} of SFO changed little following CIE. Randomization of FA distribution within and among TAG molecules of PO and PKOo led to modification in TAG composition of the PO/PKOo blends and improved miscibility between the two fats and consequently diminished the eutectic interaction that occurred between PO and PKOo.

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KEY WORDS: Chemical interesterification, DSC melting and partial melting enthalpies, palm kernel olein, palm oil, sunflower oil.

Most native fats and oils have limited applications in their unmodified forms, imposed by their TAG and FA compositions. To widen their use, they may be modified by blending, fractionation, interesterification (IE), hydrogenation, or combinations of these processes (1). Changing the natural physical characteristics of a fat or oil offers greater functionality for a large number of product formulations (2,3).

Blending is the simplest modification. As requirements for fat products become more sophisticated, however, there are correspondingly fewer ways that appropriate specifications can be met by simply blending natural fats and oils. Other modification techniques need to be used for one or more of the blend components to meet product specifications at the lowest cost (3). Hydrogenation of polyunsaturated vegetable oils is currently less appealing because of evidence that *trans* FA have adverse nutritional effects (4,5). IE has received much atten-

tion in the edible oil industry as an alternative method to improve the physical properties of fats and oils.

IE involves interchanging FA within and between TAG molecules that make up fats and oils and leads to an increased number of TAG types. Thus, important physicochemical properties, such as melting and crystallization behaviors of the fats and oils, are modified. The precise effect of IE on the properties of fat and oil depends very much on the type of starting material that is subjected to IE. For instance, the m.p. and solid fat content of a high-melting fat would be reduced when it is interesterified (IEed) with a liquid oil (2). Two types of IE are currently in commercial use, i.e., chemical (CIE) and enzymatic (EIE). CIE and random EIE using nonspecific lipases lead to a random distribution of FA on the TAG (6). In contrast, in using a 1,3-specific lipase, only the FA in the 1,3-positions are shifted; the 2-position is unchanged. Preservation of the 2-position means that a more natural fat is produced and results in the production of a much smaller absolute number of TAG compared with CIE and random EIE. Generally, EIE has certain advantages over CIE, such as milder reaction conditions and regiospecificity (7), and is currently a cost-effective alternative to CIE (8).

Palm oil (PO), an important edible oil source for the food industry, tends to crystallize as β' and therefore is an attractive option for the production of yellow fat spreads. For the production of such products, however, PO is normally combined with other fats and/or oils because PO alone does not result in products that melt quickly on the palate (9,10). Hence, PO may be blended and/or IEed with a lauric fat that contains short- and medium-chain FA and/or a liquid vegetable oil to give blends with improved melting properties. Lauric fats are often used as one component of a blend to provide a broader spectrum of chain lengths, to provide a concentrated source of saturates, or to achieve both goals. A liquid vegetable oil is always used to provide a source of unsaturated FA (3).

The aim of the present work was to investigate the effects of blending and CIE on the melting behavior of PO, sunflower oil (SFO), palm kernel olein (PKOo), and blends thereof in various ratios. The melting behaviors of the oils/fats and their blends were studied by using their DSC melting thermograms. The DSC melting thermogram gives valuable information on the melting profile of fats, e.g., on how they melt in the mouth during mastication. It can also be used to monitor the physical

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Trans-Free Fats With the Products of the Oil Palm – a Selective Review

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Abstract

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The results of nutritional research on fatty acids have led to the recommendation that the level of trans-fatty acids in foods (the products of partial hydrogenation of oils) should be reduced as far as possible. Palm oil and palm kernel oil are readily available and economical sources of solid fat. Formulae using oils to make fats for the main types of food products are reviewed.

Keywords: trans-free fats; palm oil; palm stearin; palm kernel oil

The subject of diet and health is one of universal interest, which has led to many scientific studies. In particular attention has focussed on the relation between fat intake and heart disease. The main effects of saturated and trans-fatty acids are on the cholesterol transport mechanism in the body. Cholesterol is complexed with lipoproteins of two main types for transport purposes. Low density lipoproteins (LDL-C) are used to move cholesterol to its sites of function whereas high density lipoproteins (HDL-C) remove excess cholesterol so that it can be metabolised and excreted. The LDL-cholesterol is implicated in the formation of deposits in the arteries which lead to coronary heart disease. The research has shown that some saturated fatty acids raise the level of LDL-C while leaving HDL-C largely unaffected, whereas trans-fatty acids (of which elaidic acid *tr*18:1 is the most important) both raise LDL-C and depress HDL-C.

Two specific studies of relevance may be mentioned. ASCHERIO *et al.* (1999) analysed the results

of nine controlled dietary studies of the effect of trans fatty acids on blood lipids. For both saturated and trans fatty acids the LDL-C:HDL-C ratio increased linearly with higher intake, but the trans fatty acid line had about twice the slope, indicating a greater adverse effect.

The second paper (SUNDRAM *et al.* 1997) describes a controlled dietary comparison of four fats: (1) hydrogenated soya bean oil (29% trans acids), (2) palm olein (zero trans), (3) a blend rich in oleic acid 18:1 (61%) with zero trans and (4) a blend rich in 12:0 + 14:0 (41%) with a total of 60% saturated acids and zero trans. The trans-rich fat significantly raised both LDL and total cholesterol relative to palm olein and to the 18:1 rich fats, and also uniquely depressed HDL-cholesterol.

In an extensive review of a number of both case – controlled and epidemiological studies ARO (1998) concluded “A high intake of trans fatty acids affects the ratio between LDL- and HDL-cholesterol in a way that is unfavourable compared with all other fatty acids”.

Current position

A general consensus has now developed among scientists that certain saturated fatty acids and trans fatty acids can have adverse health effects. As a result international and national bodies have made dietary recommendations in respect of trans fatty acids. The World Health Organisation recommends that consumption should be below 1% of energy intake, while in the United Kingdom the recommended limit is 2% of energy, whereas in the USA the Department of Agriculture and the US Academy of Sciences both advise a level “as low as possible”. This advice has been followed up in the USA by labelling regulations which came into force on 01/01/2006, requiring the content of trans fatty acids of food products to be declared separately on the panel of nutritional facts. This change is expected to influence consumers purchasing of oils and fats. As a result the US food industry has reformulated many of its products. In Western Europe the trans fatty acid content of food products has already been reducing for some years.

The technical problem

The results of the nutritional research and the strong official recommendations present the technologists in the food industry with a problem. Historically, the fat consumption of Northern Europe was largely based on the fats obtained from animal husbandry, that is butter, beef fat and lard. These fats have a content of saturated fats sufficient to make them solid at room temperature. Traditional foods of the region are based on this characteristic. Thus for example, butter is spreadable on bread,

lard mixed into flour is the basis for short pastry, and butter can be aerated with sugar, flour and eggs as the basis of a large variety of cakes. Liquid vegetable oils were unable to fulfil these functions, until the advent of hydrogenation at the start of the 1900s enabled them to be partly saturated, thus becoming solid to varying degrees. An intermediate step in the hydrogenation of a fatty acid is the isomerisation of a cis- into a trans-double bond. Partly hydrogenated oils inevitably have varying levels of trans fatty acids.

Oleic acid (m. pt. 12°C) is transformed into elaidic acid (m. pt. 44°C) and then into stearic acid (m. pt. 70°C).

Elaidic acid or stearic acid promote a solid character to glycerides of which they are part. However, stearic acid with its high melting point soon gives a waxy character to the fat, if present at a higher level. In contrast elaidic acid has a melting point nearer to body temperature, and has therefore always been regarded as a useful component even at a fairly high level.

In the present situation technologists have to rethink their formulae. The following options are available to achieve the solid fat characteristics needed for making traditional food stuffs.

Natural sources of solids

Beef fat however animal fats with their cholesterol content are not favoured by consumers.

The products of the oil palm – palm oil and palm kernel oil. They are readily available on the world market. Current world production of palm oil is close to 30 million tons, with 80% being exported.

Table 1. Typical solid fat content percentage by NMR of palm oil products

Temperature (°C)	Palm oil	Palm olein	Palm stearin		Palm mid fraction*
			hard	soft	
10	50.3	37.0	82.6	75.9	89.9
20	23.3	5.9	72.4	56.7	82.6
25	13.7	2.0		43.9	50.2
30	8.5		57.9	33.4	0
35	5.8		50.2	26.2	0
40	3.5		42.1	19.4	
50			24.7	6.6	
55			10.2		

*data for palm mid fraction from Britannia Food Ingredients by permission

Table 2. Physical properties of refined palm kernel oils

Solid fat content % by NMR	Palm kernel oil	Palm kernel olein	Palm kernel stearin
5°C	72.8	65.6	93.2
10°C	67.6	56.9	91.6
15°C	55.7	40.4	90.1
20°C	40.1	20.9	82.8
25°C	17.1	1.4	68.2
30°C			34.6
Slip melting point (°C)	27.3	23.6	32.2

NMR– nuclear magnetic resonance; data from Palm Oil Research Institute of Malaysia, with permission

Seed oils from some tropical trees, for example illipe nut, sal fat, shea nut. They have a solid character, but are in very limited supply.

Complete hydrogenation of a liquid vegetable oil will result in a fat of high melting point with zero trans fatty acids. In practice it can be used in food fats after interesterification with a soft oil.

Plant breeders are seeking to modify the oil consumption of several liquid oils towards a higher content of stearic and palmitic acid. No such products are available in quantity at present.

This review describes the properties of palm oil and palm kernel oil products available followed by formulae for various oil and fat products for which performance date is available.

Palm oil products

Palm oil is readily fractionated into a high melting point and a low melting point fraction, the stearin

and olein. A second fractionation can yield a mid fraction. The standard process involves crystallisation at a controlled temperature (say 22°C) followed by separation of the liquid fraction, most usually in a plate and frame filter press. Today the membrane filter press is widely used. An elastic membrane is fitted within each chamber of the press, a pressure of 5–15 bar is applied to give an efficient separation of the liquid phase. It is found that the olein is of rather uniform composition, whereas the properties of the stearin vary depending on the process conditions, particularly in the filtration. Table 1 shows the solid fat contents of palm oil products. On a second fractionation an olein of a lower solids content and a very hard stearin can be obtained if desired.

Figure 1 shows sold fat contents graphically for a similar set of samples (DE MAN & DE MAN 1994). Additionally a double fractionated palm olein of much lower solid fat content is shown.

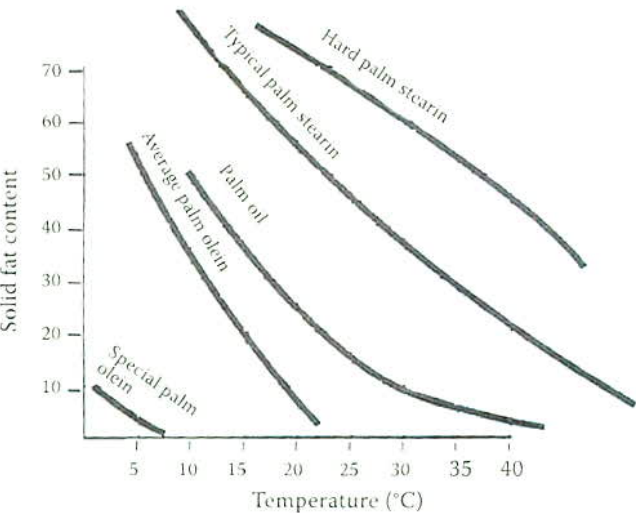


Figure 1. Solid fat content of palm oil product as determined by the IUPAC method

Table 3. Solid fat content (in %) of further processed palm kernel oil products

Temperature (°C)	Melting point (°C)		
	44.5 (fully hydrogenated palm kernel olein)	35.6 (same interesterified)	37.5 (palm kernel stearin fully hydrogenated)
10	90	82	–
15	82	74	–
20	72	60	90
25	64	45	84
30	38	25	38
35	22	6	17
37	18	3	4
40	13		3

The solid fat contents of palm kernel oil and its fractions are given in Table 2 (SIEW & BERGER 1981), while the data for further processed palm kernel oil fractions are given in Table 3 (TANG *et al.* 1999).

Because of their steep solid fat content/temperature profile, the various palm kernel oil products are useful in confectionary manufacture.

Formulation – margarine

The solid fat profile of palm oil is quite close to that of butter and it is therefore highly suitable for use in margarine. Quoting from a 1969 textbook on margarine “the number of possible combinations of oils is unlimited” (FERON 1969).

Furthermore, different markets and different manufacturers have varying concepts of the optimum product characteristics. Therefore a range of suitable formulae have been published.

Table 4 gives three formulae for packet margarines (spreadable at 20°C).

The use of palm kernel products with their high content of medium chain fatty acids gives the blend a rapid melt down and a mouth-feel similar to butter.

Blends containing a high proportion of palm oil crystallise somewhat slowly and this may result in some hardening and loss of spreadability on storage. This effect can be avoided by increasing the residence time in the scraped surface heat exchanger or by increasing its surface area by about 30% (DUNS 1985). The slow crystallisation is inherent in the glycerides of palm oil, and does not occur in interesterified blends.

The experimental margarine blend (2) in Table 4 was tested with a cone penetrometer over six weeks storage at 20°C. It showed no change and remained of good consistency (as defined by HAIGHTON 1965).

Formulae for soft tub margarines

DE MAN *et al.* (1991) found that the following blend was suitable for the Canadian market:

Table 4. Oil blends for packet margarine

Component	(1)	(2)	(3)
Liquid oil	40	30	60
Palm olein	–	40	
Palm stearin (a)	–	10	
Palm kernel oil	10		
Blend (b)	50		40
Palm oil	–	20	
Solid fat content %	5°C	58	40
	10°C	–	28
	15°C	–	18
	20°C	20	8.5
	25°C	–	5
	30°C	7	2.5
	35°C	2.5	2.1
Reference	BERGER (1986)	ÖZAY <i>et al.</i> (1998)	BERGER (1986)

(a) stearin of Iodine value 37; (b) 30 parts palm kernel oil and 70 parts palm stearin (Iodine value 41) interesterified

Palm oil	7
Fully hydrogenated palm kernel oil	8
Sunflower oil	85

The margarine had a satisfactory texture and a stable β' structure, with only 0.6% trans fatty acids.

Analysis of a tub of margarine on the market in Malaysia (IDRIS *et al.* 1996) showed the following composition:

Palm oil	74%
Palm kernel oil	12%
Soyabean oil	14%

It had the following physical characteristics:

	Yield value (N/cm ²)	Solid fat content (%)
At 5°C	16.1	33.7
At 10°C	9.8	28.9

TEAH and AHMAD (1991) reported a tub margarine formula suitable for the Japanese market:

Soft palm stearin	60 parts
Palm kernel olein	20 parts

This blend was interesterified, then blended with 20 parts sunflower oil and processed into margarine on a Schröder kombinator. The physical characteristics of the product are shown in Table 5.

The properties of interesterified blends with various palm oil products are shown in Table 6. These blends are suitable for dilution with liquid oil before processing into margarine (BERGER 1986).

While the term ‘margarine’ usually implies a fat content of 80%, many products of reduced content are offered with the description of spreads. NOOR LIDA and RAHIM (1998) analysed products from the market containing 40–60% fat to define the range of physical properties being offered and developed formulae with similar behaviour.

For block spreads in packets the conditions were satisfied by blends in the range between palm oil 80%, palm kernel olein 10% and sunflower oil 10% and palm oil 75% with sunflower oil 25%. Alternatively, interesterified palm olein or an interesteri-

fied blend of 80% palm olein with 10% palm kernel olein and 10% sunflower oil were satisfactory. The compositions intermediate between these two extremes also satisfied the criteria.

For spreads in tubs, blends of between 50% palm oil with 50% sunflower oil, and 25% palm oil with 75% sunflower oil were suitable. Using interesterification, a blend of 75% palm olein with 25% sunflower oil and one of 50% palm oil with 50% sunflower oil were suitable.

Bakery shortening

Several palm oil based formulae were tested in practical baking tests (IDRIS *et al.* 1989). A madeira cake recipe was selected which had a relatively low fat content (10.5%). The test therefore put emphasis on the capability of the fat to develop the required aerated structure. Baking tests on brands of shortening available in the supermarket led to the selection of the best performing product in terms of cake volume and crumb structure as the control for comparison. Table 7 below shows the experimental formulae, with the baking test results expressed as a percentage of the control result. In each experiment the experimental and control cakes were prepared and baked side by side. This method eliminated factors of variability in the process.

It is of interest to note the change in the physical properties of palm olein on interesterification. The reaction results in the formation of a significant amount of tripalmitin and a very different solid fat content profile, as shown in Table 8.

The shortenings shown in Table 7 are also suitable for the preparation of short pastry and for biscuits, though for some products a small increase in the proportion of liquid oil may be needed.

Frying fats

The manufacture of starch based snack foods such as potato crisps, and of convenience foods

Table 5. Physical characteristics of tub margarine

Temperature (°C)	Solid fat content (%)	Yield value (g/cm ²)
10	16.0	450
15	14.0	–
20	11.0	200
30	5.9	–

Table 6. Randomised blends for margarines

	Composition					
	POS:PKOF (60:40)	PO:PKO (80:20)	POF:PKO (90:10)	POS:SBO (40:60)	POS:RSO (L.E.) (40:60)	POS:CSO (20:80)
M. Pt (°C)	35.5	35.5	33.2	32.3	36.0	34.0
SFC (%)						
10°C	52.7	57.5	41.6	17.5	19.4	18.7
15°C	43.7	49.5	30.2	10.7	12.7	10.3
20°C	30.0	37.1	20.8	5.9	9.6	6.5
25°C	19.3	25.8	13.8	3.9	5.7	3.7
30°C	11.4	17.4	7.8	2.5	3.7	2.8
35°C	3.8	9.3	4.3	0.8	3.6	2.2
37°C	0.4	4.3	2.3	0.9	2.3	1.1
40°C	–	2.6	0.8	–	1.6	0.4

POS = Palm stearin (Iodine value 50); PKOF = Palm kernel olein; SBO = Soyabean oil; RSO (L. E.) = Low erucic rapeseed oil; CSO = Cottonseed oil

involves frying in large continuous fryers containing 1–2 tonnes of fat. Resistance to oxidation during extended use is necessary and has led in part to the use of partly hydrogenated vegetable oils. Palm oil or palm olein, with their good resistance to oxidation are today used world wide for industrial frying (BERGER 2005) with an estimated use of between 5 and 10 million tonnes/year. Their satisfactory performance in potato crisps (DU PLESSIS & MEREDITH 1999; MARTIN-PORVILLO *et al.* 1996; HAMMOND 2002) and in prefried French fries has been reported (SEBEDIO *et al.* 1991).

In the author's experience palm oil proved satisfactory over a period of years in the frying of doughnuts. For this product, a fat that is solid at room temperature is needed to enable the sugar glaze to adhere to the surface.

Vanaspati

In the Indian subcontinent and in the Middle East butter does not have sufficient keeping properties due to the high ambient temperatures. Traditionally therefore an anhydrous butterfat is prepared. In the 1930's a replacement was developed in India, by partial hydrogenation of vegetable oil to have melting characteristics and the coarse crystal structure of butter. This required selective hydrogenation and a high trans fatty acid content (35% trans in India, up to 50% trans in Iran.) Trans free blends of palm stearin with liquid oil have been proposed (RAY & BHATTACHARYYA 1996; NOR AINI *et al.* 2001; MAYAMOL *et al.* 2004). 40–60% stearin is used, depending on the grade of stearin.

An interesterified blend of 70 parts palm stearin (Iodine value 45, melting point 49.6°C) and 30 parts

Table 7. Bakery shortening formulae

Component	Blend	Interesterified blend	Interesterified
Palm stearin (Iodine value 44)	60	70	–
Low erucic rape oil	40	–	–
Soybean oil	–	30	–
Palm olein	–	–	100
Relative specific volume	100	100 ^a , 100 ^b	99 ^a , 98 ^b

^amixing operation at 20°C; ^bmixing operation at 27°C

Table 8. Effect of interesterification on the solid fat content (%) of palm olein

Temperature (°C)	Before esterification	After interesterification
10	38.2	49.9
15	19.9	37.4
20	5.7	28.9
25	2.1	19.3
30	–	12.8
35	–	10.6
40	–	6.8

Soya bean oil had good crystallising properties and a melting point of 41°C, suitable for India (KHEIRI 1985).

Bakers whipping cream

Whipped dairy cream has inadequate stand-up properties in summer weather. An interesterified blend of 34 parts of fully hydrogenated palm kernel oil (Iodine value 1.0) with 66 part of palm stearin (Iodine value 19.0), has superior stability. The blend was used in a proprietary baker’s cream formula. The cream was aerated to a density of 0.34 and stored at temperatures between 25°C and 40°C. The cream remained completely stable for 4 h at up to 37°C and after 20 h at that temperature showed only minimal change (NESARETNAM *et al.* 1993). Firmness measured with a cone penetrometer, and mouth feel were judged to be satisfactory.

An interesterified blend of palm stearin with palm kernel olein is suitable for various confectionery applications (TIMMS 2003). Table 9 shows the solid fat content of a blend of equal parts of palm stearin (Iodine value 35) and palm kernel olein (Iodine value 22.5).

Conclusions

The adverse effects of trans fatty acids on blood lipids have led the World Health Organisation and national governments to recommend that the intake of trans acids should be reduced. The requirement in many food products for a consistent fat with a solids content at ambient temperature has in the past been largely satisfied by formulations containing partly hydrogenated vegetable oils. This has resulted in margarines and shortenings with trans fatty acid

Table 9. Solid fat content (%) of palm stearin-palm kernel olein blend

Temperature (°C)	Before interesterification	After interesterification
10	61.0	68.0
15	39.0	57.5
20	25.0	44.0
25	18.0	29.0
30	15.0	12.0
35	12.5	1.5
40	11.0	Nil
45	7.5	–

contents in the range of 10–30%. Reformulation to minimise trans content can be achieved by using the natural solid fat content of palm and palm kernel oils. Palm oil is readily fractionated to give an olein, liquid at 20°C, and a stearin, which can have a range of properties according to the fractionating conditions. Palm kernel oil is fractionated to give a stearin of low Iodine value with properties very useful in confectionary products, while the olein is useful in margarine blends. Numerous published formulae for margarines and reduced fat spreads use blends containing palm oil, and/or palm stearin, with palm kernel oil and a liquid oil. Often some components are interesterified before use in the final blend. Bakery fats using palm oil based blends give results in cakes and pastry equal to established commercial products. Aerated bakery creams using interesterified palm stearin with fully hydrogenated palm kernel oil had good eating quality. The formula could be adjusted for stability at higher ambient temperatures by a small increase in the proportion of stearin. Palm oil and palm kernel olein are used world-wide for industrial frying of snack foods, in fast food restaurants and domestically, having excellent high temperature stability.

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Fraccionamiento e interesterificación del aceite de palma (*Elaeis guineensis*) cultivado en la amazonia peruana

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RESUMEN

Fraccionamiento e interesterificación del aceite de palma (*Elaeis guineensis*) cultivado en la amazonia peruana.

En el presente trabajo se realizó el estudio de las características físicas y químicas del fruto de la palma aceitera procedente de la cuenca del Maniti. (Región Loreto - Perú). Del mismo modo se realizó el fraccionamiento e interesterificación de las mezclas de aceite de palma y estearina en las proporciones. Sobre el aceite crudo y los productos se determinaron las propiedades físico-químicas y análisis de ácidos grasos mediante la cromatografía gaseosa. El aceite de palma presenta una concentración de ácido grasos saturados de 51,17% y cuando fraccionado a 25 °C, este se incrementa en la estearina a 54,31%. Los mejores productos para la industria de alimentos son las mezclas interesterificadas de estearina tanto sola como con sus mezclas con aceite de palma, dado que presentan puntos de fusión próximos a 37 °C.

PALABRAS-CLAVE: Aceite de palma – *Elaeis guineensis* – Fraccionamiento – Mezclas – Interesterificación.

SUMMARY

Fractionation and interesterification of palm (*Elaeis guineensis*) oil from Peruvian Amazon

In the present work, the physical and chemical characteristics of the fruit of the oily palm coming from the river basin of the Maniti (Region Loreto - Peru) were studied. Also, the fractionation of the palm oil and the interesterification of mixtures of palm oil/stearin was carried out. Physico-chemical properties of the crude oil and of the products obtained and fatty acids were analysed by gas chromatography. The level of saturated fatty acids increased from 51,17% in the palm oil to 54,31% in the stearin. The best products for the food industry were the interesterified samples as they had melting points close to 37 °C.

KEY-WORDS: *Elaeis guineensis* – Fractionation – Interesterification – Mixtures – Palm oil.

1. INTRODUCCIÓN

La palma aceitera (*Elaeis guineensis*) es una palmera originaria de los trópicos del África, cuyo

fruto da un aceite de optima calidad, con alta concentración de ácidos palmítico y oleico y que con las técnicas de modificación adecuadas permite obtener una amplia variedad de productos para la industria de alimentos, entre los cuales se encuentran los aceites de cocina, mantecas, bases para margarinas, "vanaspati" (grasa vegetal sustituto de la mantequilla en la cocina) y, para la industria oleoquímica, materias primas para la fabricación de jabón, jabones metálicos, velas, y grasas lubricantes (Berger y Ong, 1985; PORIM, 1988; Boza, 1990). Esta palmera se encuentra actualmente siendo cultivada en las regiones de San Martín y Loreto, e incluso el estado peruano ha declarado su cultivo de interés nacional (Perú, 2000).

La siembra de palma aceitera en la cuenca del Maniti (Región Loreto-Perú) se inició en el año de 1981, con la firma del convenio entre ORDELORETO (Organismo de desarrollo de Loreto) y la empresa EMDEPALMA (Empresa para el desarrollo y explotación de palma aceitera), ubicando y desarrollando los viveros y parcelas en el caserío de Santa Cecilia.

El fraccionamiento del aceite es considerado como un proceso de modificación termomecánico, donde los triglicéridos componentes del aceite son separados generalmente como una mezcla de cristalización parcial, en una fase líquida (oleína) y otra sólida (estearina) (Thomas III, 1985). Se han desarrollado diferentes métodos para el fraccionamiento de aceites, principalmente con el objetivo de modificar su textura y punto de fusión. Esta técnica permite aislar las diversas clases de triglicéridos sin cambiar la distribución de la posición de los ácidos grasos y su utilización en la industria se da en el caso de obtener sucedáneos de la manteca de cacao, obtención de aceites láuricos a partir del aceite de coco y fraccionamiento de la grasa de leche (Willis et al., 1998).

La mezcla de aceites y grasas permite obtener productos finales con características propias. Ello podría ser considerado como un método de modificación de aceites y grasas, sobre todo debido a las

interacciones que tienen lugar entre los triglicéridos que promueven alteraciones en las propiedades físicas de los productos oleosos (Smalwood, 1989; Birker y Padley, 1987).

La interesterificación es un proceso que modifica la distribución natural de los ácidos grasos en las moléculas de los triglicéridos. La composición de los ácidos grasos permanece idéntica a la grasa o mezcla original, pero las propiedades físicas, como punto de fusión, contenido de grasa sólida y forma de cristalización, son modificadas (Gioielli, 1996; Sonntang, 1982).

La interesterificación puede realizarse por simple calentamiento de los aceites y grasas a temperaturas que bordean los 300 °C, pero la reacción a esta condición es lenta y normalmente acompañada de descomposición y polimerización de los triglicéridos. En la industria se utilizan catalizadores para disminuir la temperatura de la reacción. Los catalizadores más usados son los metales alcalinos y sus derivados, siendo el metóxido de sodio el más empleado, debido a sus ventajas de costo, manipulación y temperatura de reacción, que puede ser reducida al rango de 30-90 °C (Gioielli, 1996; Hurtová et al., 1996).

El objetivo del presente trabajo fue el de realizar los análisis físicos y químicos del fruto, así como efectuar la modificación del aceite de palma mediante el fraccionamiento, mezclas e interesterificación con los frutos procedentes de la cuenca del Maniti-Región Loreto-Perú.

2. PARTE EXPERIMENTAL

2.1. Muestras y tratamientos

Se utilizaron frutos de palma aceitera (Elaeis guineensis) recolectados de los sectores Paparo y Paparillo, en el Distrito de Indiana, Provincia de Maynas, Región Loreto, distante a unos 80 Km de la ciudad de Iquitos, zona de la Cuenca del Maniti.

Los frutos fueron llevados a una pequeña planta extractora en la misma zona de recolección y primero se sometieron a cocción por aproximadamente tres horas y posteriormente, se extrajo el aceite con una prensa manual. Este aceite fue sometido a:

- a) **Fraccionamiento:** El aceite se colocó en cinco vasos de precipitado de 100 mL y se colocaron en baños a temperaturas de 15, 20, 25 y 30 °C por tres horas. De inmediato los productos fueron filtrados a temperatura ambiente, obteniéndose las fracciones de oleica (parte líquida) y estearina (parte sólida).
- b) **Mezclas:** Se realizaron mezclas binarias del aceite de palma con su estearina en diferentes proporciones de acuerdo al diseño experimental indicado en la Tabla 1.
- c) **Interesterificación:** Las mezclas se sometieron a la reacción de interesterificación, para lo cual se utiliza como catalizador el metóxido de sodio en la concentración de

Tabla 1
Diseño experimental de las mezclas de aceite de palma y de su estearina

Número de muestra	Proporción de aceite de palma x ₁	Proporción de estearina x ₂
1	1	0
2	0	1
3	2/3	1/3
4	1/3	2/3

0,75% en peso con respecto al peso de la mezcla, de acuerdo a Sotero-Solis et al. (2001).

2.2. Determinaciones analíticas

Los análisis de composición proximal se realizaron según las Normas del Instituto Adolfo Lutz (1976), que incluyó los análisis de humedad, proteína, aceite y fibra. La concentración de carbohidratos fueron obtenidos por la diferencia de 100 menos la suma de los porcentajes de agua, proteína, aceite y ceniza. Para la caracterización de los aceites se determino el punto de fusión, densidad, índices de refracción, de acidez y de yodo, según los métodos de la AOAC (1995). La concentración de β-caroteno por el método espectrofotométrico, según Higby (1962). La composición de ácidos grasos se determinó de acuerdo al método de Hartman y Lago (1973).

Para el análisis de composición de los ácidos grasos se utilizó el cromatógrafo de gas marca Shimadzu, modelo CG17A, utilizando una columna capilar de sílica fundida VA-WAX (polietilenglicol) de 30 m de largo y 0,25 mm de diámetros interior, el gas de arrastre fue helio con flujo de 1 mL/minuto. La programación de temperatura en la columna fue isotérmica a 150 °C por 11 minutos y la velocidad de calentamiento 3 °C/min. hasta 210 °C, permaneciendo por 5 minutos, siendo que la temperatura de vaporización fue de 250 °C y la del detector de 280 °C.

3. RESULTADOS Y DISCUSIÓN

En la Tabla 2, se presenta las características físicas del fruto así como su análisis proximal. El tamaño y peso del fruto es de 4,22 cm y 14.29 g con muy poca variación entre la población muestreada. El peso de la pulpa y semilla con relación al fruto es de 72,36% y 27,71% respectivamente. Estos datos corresponden a la variedad denominada "Dura" según Boza (1990) y que a pesar de no haber mantenido un adecuado manejo, aún conserva las características propias de esta. Asimismo, se observa que la concentración de aceite en la pulpa es de 69,21% lo que representa en el fruto la cantidad de 50% de aceite en fruto, un poco superior al obtenido por la empresa Palma del Espino del Perú (Hidalgo, 2005), quienes reportan 45%.

Tabla 2
Características físicas y composición proximal del fruto de la palma aceitera (*Elaeis guineensis*), del Maniti

Características físicas	Media
Longitud del fruto (cm)	4,22 ± 0,50
Diámetro del fruto (cm)	2,76 ± 0,30
Peso del fruto (g)	14,29 ± 3,77
Peso de la pulpa (g)	10,31 ± 2,65
Longitud de la semilla (cm)	3,04 ± 0,34
Diámetro de la semilla (cm)	1,79 ± 0,31
Peso de la semilla (g)	3,96 ± 1,31
Composición proximal	
Humedad, g/100g	13,08 ± 0,09
Ceniza, g/100g	0,26 ± 0,02
Aceite, g/100g	69,21 ± 0,11
Proteína, g/100g	1,86 ± 0,01
Fibra, g/100g	4,56 ± 0,01
Carbohidratos, g/100g	11,03 ± 0,01

La Tabla 3 muestra los ensayos y el rendimiento de oleína y estearina obtenidos tras el fraccionamiento en seco del aceite de palma a cuatro temperaturas diferentes, se observa que a 25 °C se obtiene un buen fraccionamiento, esta temperatura difiere con la reportada por Thomas III (1985) quienes indican que el fraccionamiento lo realizaron a 10 °C y 20 °C. Esta diferencia se debe, posiblemente, a que ellos trabajaron el fraccionamiento con solvente.

En la Tabla 4, se presentan las características físico-químicas del aceite de palma y sus productos de fraccionamiento, así como la concentración de caroteno y retinol de los mismos, se observa que

Tabla 3
Ensayos del fraccionamiento del aceite de palma a diferentes temperaturas

Temperatura (°C)	Estearina (%)	Oleína (%)
15	100,00	0,00
20	100,00	0,00
25	78,75	21,25
30	76,00	24,00

Tabla 4
Características físico químicas, β-caroteno y retinol del aceite de palma y de los productos del fraccionamiento

Determinaciones	Aceite de palma	Oleína	Estearina
Punto de fusión, °C	13,50	—	28,00
Densidad, g/mL	0,9151	0,9165	0,9019
Índice de refracción	1,4605	1,4660	1,4629
Índice de saponificación	204,35	203,44	204,66
Índice de Iodo	50,48	54,34	46,86
β-Caroteno, mg/100g	0,359	0,355	0,361
Retinol, mg/100g	2,520	2,529	2,613

comparando a la estearina con el aceite original esta incrementa notablemente su punto de fusión, alcanzando 28 °C, así como una ligera disminución de la densidad y la mejora en la concentración de β-caroteno y retinol. Como era de esperar la estearina presenta un menor índice de iodo debido al menor número de insaturaciones en las moléculas de sus ácidos grasos.

Observando la Tabla 5, donde se reporta la concentración de ácidos grasos para el aceite de

Tabla 5
Composición de ácidos grasos del aceite de palma y de los productos del fraccionamiento

Ácido graso	Aceite de Palma	Oleína	Estearina
12 : 0	0,05 ± 0,02	0,05 ± 0,01	0,03 ± 0,02
14 : 0	1,14 ± 0,09	1,13 ± 0,05	1,19 ± 0,06
15 : 0	0,03 ± 0,02	0,03 ± 0,02	0,05 ± 0,01
16 : 0	45,24 ± 0,13	41,86 ± 0,11	48,22 ± 0,07
16 : 1	0,19 ± 0,03	0,20 ± 0,01	0,17 ± 0,01
17 : 0	0,13 ± 0,05	0,09 ± 0,00	0,10 ± 0,01
18 : 0	4,13 ± 0,10	3,91 ± 0,06	4,24 ± 0,04
18 : 1 (n-9)	36,50 ± 0,48	39,51 ± 0,17	34,72 ± 0,22
18 : 1 (n-7)	0,73 ± 0,01	0,80 ± 0,02	0,69 ± 0,01
18 : 2 (n-6)	10,60 ± 0,46	11,30 ± 0,16	9,44 ± 0,07
18 : 3 (n-3)	0,28 ± 0,02	0,30 ± 0,01	0,25 ± 0,01
20 : 0	0,36 ± 0,01	0,35 ± 0,01	0,36 ± 0,01
20 : 1 (n-9)	0,12 ± 0,02	0,12 ± 0,01	0,10 ± 0,01
22 : 0	0,04 ± 0,04	0,06 ± 0,01	0,06 ± 0,01
22 : 1 (n-9)	< 0,04	< 0,03	< 0,03
22 : 2 (n-6)	0,19 ± 0,01	0,20 ± 0,01	0,21 ± 0,03
24 : 0	0,05 ± 0,04	0,06 ± 0,00	0,07 ± 0,01
n.i.	0,22 ± 0,15	0,03 ± 0,09	0,10 ± 0,03
Saturados	51,17 ± 0,18	47,54 ± 0,15	54,31 ± 0,09
Monoinsaturados	37,54 ± 0,43	40,62 ± 0,15	35,68 ± 0,23
Poliinsaturados	11,08 ± 0,46	11,80 ± 0,17	9,90 ± 0,11

n.i: no identificados.

palma, oleina y estearina, obtenidos por cromatografía gaseosa, se puede observar que la concentración de ácidos grasos del aceite crudo de palma, no difiere de forma importante de los indicados por Berger y Ong (1985), quienes realizaron análisis al aceite de palma procedente de Malasia, destacando siempre la presencia de ácido palmítico (45,24%), oleico (36,50%) y linoléico (10,60%). Asimismo la estearina presenta una mayor concentración de ácidos grasos saturados (54,31%) que el aceite crudo de palma (51,17%) y su oleina (47,54%).

De acuerdo a la Tabla 6, donde se reporta las propiedades físico-químicas de los productos antes y después de la interesterificación, no se observa grandes diferencias en los índices de yodo y saponificación, así como con la densidad e índice de refracción. Esto se debe a que en las reacciones de interesterificación, solamente hay un rearreglo molecular de los ácidos grasos en torno de la molécula de glicerol (Gioielli, 1996; Sonntang, 1982). En cuanto a las variaciones de los puntos de fusión antes y después de la interesterificación, concuerdan con lo afirmado por Sonntang (1982), quien indica que en muestras de bajo punto de fusión este aumenta después de la interesterificación; lo cual también fue reportado por Sotero-Solis et al. (2001) al trabajar con mezclas del aceite de castaña y su grasa hidrogenada. De este modo se observa que la estearina de palma interesterificada, así como las proporciones de mezcla de estearina y sus mezclas con aceite de palma, mantienen un punto de fusión muy próximo al de la temperatura del cuerpo humano, lo cual los vuelven productos interesantes para la industria alimenticia en cuanto serviría para la preparación de margarinas, helados y productos de panificación. Según los resultados de los análisis de β-caroteno y retinol, se observa que no hubo degradación de estos compuestos cuando fue sometido a la reacción de interesterificación. Las concentraciones de β-carotenos guardan concordancia con los obtenidos por Choo et al. (1993) quienes efectuaron análisis de aceite de palma procedente de Malasia.

En la Tabla 7 se presenta la composición de ácidos grasos de las mezclas antes de ser interesterificadas y en la Tabla 8 después de esta reacción. No se observa mayor diferencia en la composición de estos compuestos al comparar los productos iniciales con los finales, debido a que solo se realizó un intercambio intermolecular de los esteres de los ácidos grasos (Sonntang, 1982) y como se indicó anteriormente, los cambios son específicamente en las propiedades físicas; aunque se observa un ligero incremento en los ácidos grasos saturados de las muestras 3 y 4, posiblemente debido al decremento de algunos ácidos grasos mono y poliinsaturados en la reacción de interesterificación.

4. CONCLUSIONES

- 1. Con el aceite crudo obtenido en la cuenca del Maniti, Región Loreto-Perú, el mejor fraccionamiento se lleva a cabo a 25 °C.
- 2. Los análisis de caracterización del aceite de palma, oleina y estearina no difieren de los presentados en los trabajos realizados con la misma materia prima en Malasia.
- 3. Con las mezclas de estearina con el aceite de palma interesterificadas, en sus diferentes proporciones, se obtienen productos que muy bien se pueden utilizar en la industria de alimentos, sea en la preparación de margarinas, helados o industria de panificación.
- 4. La presencia de β-caroteno indican una excelente concentración de estos importantes compuestos, útiles tanto como vitamina así como antioxidantes.

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Tabla 6
Características físico-químicas, β-caroteno y retinol de las mezclas antes y después de la interesterificación

Determinaciones	Muestras							
	Sin Interesterificar				Interesterificadas			
	1	2	3	4	1	2	3	4
Punto de fusión	13,50	28,00	21,33	19,50	43,17	38,33	40,00	36,83
Densidad	0,9151	0,9019	0,9010	0,9021	0,9192	0,9134	0,9057	0,9072
Índice de refracción	1,4605	1,4629	1,4628	1,4641	1,4630	1,4630	1,4651	1,4646
Índice de saponificación	204,35	204,66	204,05	204,10	203,84	203,09	203,19	203,18
Índice de Iodo	50,48	46,86	46,99	47,98	53,47	47,90	47,86	47,82
β-Caroteno, mg/100g	0,359	0,361	0,362	0,366	0,356	0,368	0,353	0,390
Retinol, mg/100g	2.520	2.613	2.560	2.580	2.515	2.624	2.509	2.585

Tabla 7
Composición de ácidos grasos de las mezclas antes de la interesterificación

Ácido graso	Muestras			
	1	2	3	4
12 : 0	0,05 ± 0,01	0,03 ± 0,02	0,05 ± 0,02	0,08 ± 0,01
14 : 0	1,13 ± 0,05	1,19 ± 0,06	1,14 ± 0,09	1,33 ± 0,08
15 : 0	0,03 ± 0,02	0,05 ± 0,01	0,03 ± 0,02	< 0,08
16 : 0	41,86 ± 0,11	48,22 ± 0,07	45,24 ± 0,13	42,84 ± 0,20
16 : 1	0,20 ± 0,01	0,17 ± 0,01	0,19 ± 0,03	0,19 ± 0,01
17 : 0	0,09 ± 0,00	0,10 ± 0,01	0,13 ± 0,05	0,12 ± 0,02
18 : 0	3,91 ± 0,06	4,24 ± 0,04	4,13 ± 0,10	3,95 ± 0,12
18 : 1 (n-9)	39,51 ± 0,17	34,72 ± 0,22	36,50 ± 0,48	38,31 ± 0,39
18 : 1 (n-7)	0,80 ± 0,02	0,69 ± 0,01	0,73 ± 0,01	0,73 ± 0,01
18 : 2 (n-6)	11,30 ± 0,16	9,44 ± 0,07	10,60 ± 0,46	11,35 ± 0,23
18 : 3 (n-3)	0,30 ± 0,01	0,25 ± 0,01	0,28 ± 0,02	0,33 ± 0,02
20 : 0	0,35 ± 0,01	0,36 ± 0,01	0,36 ± 0,01	0,35 ± 0,01
20 : 1 (n-9)	0,12 ± 0,01	0,10 ± 0,01	0,12 ± 0,02	0,12 ± 0,02
22 : 0	0,06 ± 0,01	0,06 ± 0,01	0,04 ± 0,04	< 0,08
22 : 1 (n-9)	< 0,03	< 0,03	< 0,04	< 0,08
22 : 2 (n-6)	0,20 ± 0,01	0,21 ± 0,03	0,19 ± 0,01	0,17 ± 0,01
24 : 0	0,06 ± 0,00	0,07 ± 0,01	0,05 ± 0,04	< 0,08
n.i.	0,03 ± 0,09	0,10 ± 0,03	0,22 ± 0,15	0,13 ± 0,00
Saturados	47,54 ± 0,15	54,31 ± 0,09	51,17 ± 0,18	48,66 ± 0,17
Monoinsaturados	40,62 ± 0,15	35,68 ± 0,23	37,54 ± 0,43	39,35 ± 0,37
Poliinsaturados	11,80 ± 0,17	9,90 ± 0,11	11,08 ± 0,46	11,85 ± 0,23

n.i: no identificados

Tabla 8
Composición de ácidos grasos de las mezclas después de la interesterificación

Ácido graso	Muestras			
	1	2	3	4
12 : 0	0,08	—	—	—
14 : 0	1,33	1,08 ± 0,00	1,09 ± 0,01	1,11 ± 0,01
15 : 0	< 0,08	—	—	0,03 ± 0,02
16 : 0	42,84	47,92 ± 0,33	47,91 ± 0,19	47,03 ± 0,01
16 : 1	0,19 ±	0,16 ± 0,00	0,15 ± 0,00	0,15 ± 0,01
17 : 0	0,12 ± 0,02	0,10 ± 0,01	0,09 ± 0,01	0,09 ± 0,01
18 : 0	3,95 ± 0,12	4,22 ± 0,01	4,33 ± 0,02	4,41 ± 0,01
18 : 1 (n-9)	38,31 ± 0,39	35,59 ± 0,26	35,33 ± 0,13	35,68 ± 0,04
18 : 1 (n-7)	0,73 ± 0,01	0,61 ± 0,01	0,58 ± 0,02	0,57 ± 0,00
18 : 2 (n-6)	11,35 ± 0,23	9,62 ± 0,08	9,74 ± 0,04	10,11 ± 0,02
18 : 3 (n-3)	0,33 ± 0,02	0,24 ± 0,00	0,23 ± 0,01	0,24 ± 0,01
20 : 0	0,35 ± 0,01	0,36 ± 0,00	0,37 ± 0,00	0,38 ± 0,00
20 : 1 (n-9)	0,12 ± 0,02	0,11 ± 0,01	0,11 ± 0,00	0,11 ± 0,00
22 : 0	< 0,08	—	0,07 ± 0,01	0,07 ± 0,00
22 : 1 (n-9)	< 0,08	—	—	0,03 ± 0,02
22 : 2 (n-6)	0,17 ± 0,01	—	—	—
24 : 0	< 0,08	—	—	—
n.i.	0,13 ± 0,00	—	—	—
Saturados	48,66 ± 0,17	53,67 ± 0,33	53,86 ± 0,20	53,12 ± 0,04
Monoinsaturados	39,35 ± 0,37	36,48 ± 0,26	36,17 ± 0,15	36,53 ± 0,03
Poliinsaturados	11,85 ± 0,23	9,86 ± 0,08	9,98 ± 0,05	10,35 ± 0,02

n.i: no identificados

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Effects of chemical interesterification on solid fat content and slip melting point of fat/oil blends

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Abstract Fat/oil blends, formulated by mixing fully hydrogenated palm oil stearin or palm oil stearin with vegetable oils (canola oil and cottonseed oil) in different ratios from 30:70 to 70:30 (w/w %), were subjected to chemical interesterification reactions on a laboratory scale. Fatty acid (FA) composition, iodine value, slip melting point (SMP) and solid fat content (SFC) of the starting blends were analysed and compared with those of the interesterified blends. SMPs of interesterified blends were decreased compared to starting blends because of extensive rearrangement of FAs among triacylglycerols. These changes in SMP were reflected in the SFCs of the blends after the interesterification. SFCs of the interesterified blends also decreased with respect to the starting blends, and the interesterified products were softer than starting blends. These interesterified blends can be used as an alternative to partial hydrogenation to produce a plastic fat phase that is suitable for the manufacture of margarines, shortenings and confectionary fats.

Keywords Chemical interesterification · Vegetable oils · Palm oil stearin · Solid fat content · Slip melting point

Introduction

Most vegetable oils in their native state have only limited applications due to their specific chemical compositions. To widen their use, vegetable oils are modified, either chemically by hydrogenation or interesterification, or physically by fractionation [1]. Interesterification is one of the most important processes for modifying the physicochemical characteristics of oils and fats [2]. During interesterification, fatty acids (FAs) are exchanged within (intraesterification) and among (interesterification)

triacylglycerols (TAGs) until a thermodynamic equilibrium is reached [3].

Interesterification of solid fats and vegetables oils can produce a fat blend with optimum characteristics. Rearrangement or randomization of acyl residues in TAGs has provided fats or oils with new physical properties [4]. In most oils and fats, unsaturated FAs preferentially occupy the 2-positions of the TAG molecules. FAs are distributed in a random manner among the TAG molecules by chemical interesterification. The degree of unsaturation or isomeric state of the FA does not change [2]. However, during partial hydrogenation, some *cis* double bonds are isomerised into their *trans* forms. In the past few years, several nutritional studies have suggested a direct relationship between *trans* FAs and increased risk for coronary heart diseases [5, 6, 7].

Palm oil (PO) and its fractions are important edible oil sources for the food industry because of advantageous properties such as high thermal and oxidative stability and plasticity. They tend to crystallize as a β crystal form, and this is important for some fat products. Moreover, the relatively slow crystallizing properties of PO and its fractions can result in a rather brittle structure. To improve the melting properties, they may be interesterified with vegetable oils or fats that contain short chain FAs [2, 8].

Solid fat content (SFC) greatly influences the suitability of oils and fats for a particular application. SFC, the amount of fat crystals in the blends, is responsible for many product characteristics including general appearance, ease of packing, organoleptic properties, ease of spreading, and oil exudation. SFC can also be used to study the compatibility of fats by determining the changes in the percentage of solids at different fat proportions [2, 8].

The objective of this study was to investigate the effects of chemical interesterification on the physical properties of fully hydrogenated palm oil stearin (FH-POS), palm oil stearin (POS), canola oil (CO) and cottonseed oil (CSO) mixed in various ratios (w/w), and

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Modificación de aceites y grasas en la industria de alimentos*

Modificaciones de aceites y grasas

Las exigencias permanentes de los consumidores y los procesos de innovación de los fabricantes de alimentos, han llevado a que se produzcan diferentes tipos de productos que cumplen no sólo requisitos de palatabilidad sino también requerimientos de salud. Es entonces importante resaltar la necesidad de que en el mercado existan diferentes productos grasos que se adapten a las necesidades de todos los órdenes alimentarios.

Para cubrir todas esas nacientes necesidades y las ya tradicionales en la industria de aceites y grasas, no es suficiente tener una amplia gama de materias primas que, solas o mezcladas con otras, ofrezcan propiedades especiales en su uso y características nutricionales específicas. Para atender los requerimientos de una creciente industria, las grasas y los aceites pueden modificarse usando procesos particulares, dependiendo de lo que busque cada fabricante, pero en especial de los requisitos de cada consumidor. Puede decirse que existen tres procesos diferentes de modificación de aceites y grasas de importancia en la industria de alimentos y con opciones de usarse incluso en oleoquímica.

Los procesos más conocidos en la modificación de aceites y grasas son la Hidrogenación, el Fraccionamiento y la Interesterificación (Figura 1). Estos procesos existen desde hace ya bastantes años y en la actualidad son los equipos los que han evolucionado así como los catalizadores de las reacciones como tal. Sin embargo, el mecanismo básico que rige el proceso sigue manteniéndose sin importantes cambios.

Hidrogenación

Se define como hidrogenación el proceso mediante el cual se saturan los dobles enlaces existentes en los triacilglicéridos inyectando hidrógeno gaseoso a los aceites o las grasas en condiciones controladas de temperatura y presión en presencia de catalizadores de tipo metálico (Figura 2). Esta reacción es selectiva y los áci-

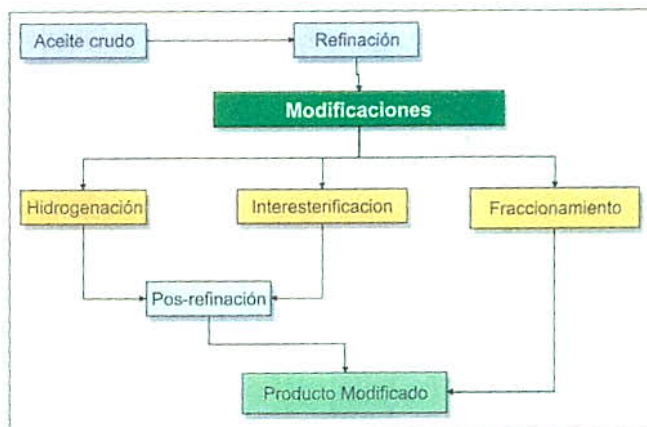


Figura 1. Procesos de modificación de aceites y grasas.

dos grasos con mayor grado de insaturación son los primeros en reaccionar. Esta característica de la reacción es aprovechada para obtener productos con características especiales a partir de hidrogenación parcial. La hidrogenación parcial genera la aparición de isómeros de posición y geométricos conocidos como ácidos grasos *trans*, los cuales poseen características especiales resaltando puntos de fusión bastante más altos que sus similares *cis*.

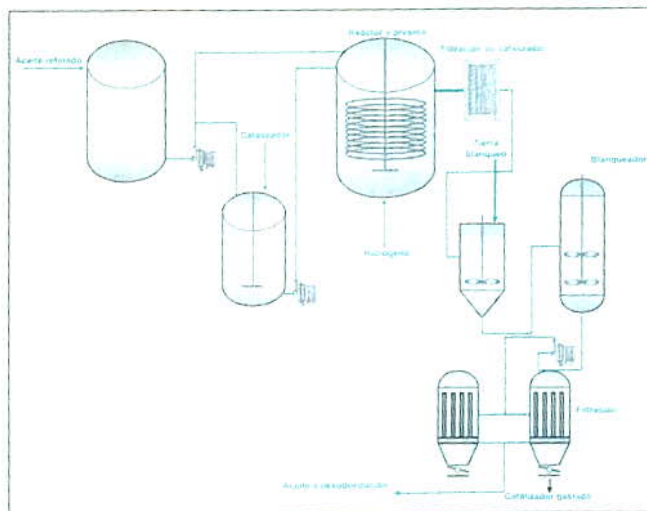


Figura 2. Hidrogenación.

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Los objetivos de la hidrogenación aplicada en los alimentos, son el aumento de la estabilidad a la oxidación de los aceites con importantes niveles de insaturación y la modificación de las propiedades de fusión de los aceites al convertirlos en grasas permitiendo su uso en aplicaciones muy particulares. Las grasas hidrogenadas pueden usarse en aplicaciones alimenticias como la producción de margarinas industriales y de mesa, grasas para rellenos, cobertura para helados e incluso para diseñar grasas usadas como sustitutos o equivalentes a la manteca de cacao. El proceso de hidrogenación total no produce ácidos grasos *trans* y efectivamente, se usa para fabricar productos de panificación y chocolatería.

Debido a los resultados de investigaciones donde se ha encontrado que el consumo de grasas *trans* tienen un efecto perjudicial para la salud, las autoridades de salud de varios países en el mundo han desarrollado acciones para obligar, a quienes usan este tipo de grasas en sus productos, a declarar su presencia en los alimentos y por esta razón los procesos de hidrogenación que producen ácidos grasos *trans* deberán ser sustituidos o modificados, de tal forma que se tengan productos sanos o con menores efectos negativos en la salud, mejorando propiedades nutricionales y de sabor y así generar aceptación en el consumidor (Cadena, 2007).

Fraccionamiento

El fraccionamiento, a diferencia de la hidrogenación y la interesterificación, es completamente reversible y se aplica a aquellos productos donde coexistan ácidos grasos saturados e insaturados, como por ejemplo los aceites de palma y palmiste. Se caracteriza porque no se dan reacciones químicas y su objetivo se logra al cristalizar por enfriamiento los triglicéridos con mayor contenido de saturados de un aceite, separándolos de los triglicéridos con mayor contenido de insaturados produciendo dos fracciones muy diferentes entre sí y además distintas del aceite o grasa original. Este proceso, normalmente conocido como arte y no como ciencia, ofrece múltiples alternativas de separación de fases (enriquecidas en saturados e insaturados) lo que al final permite tener también una alta variedad de productos. El proceso convencional, aplicado a aceite de palma (crudo o refinado), se ha desarrollado también en equipos que evolucionan buscando mayores rendimientos de las fracciones de interés por parte del procesador.

Actualmente, las plantas de fraccionamiento pueden separar en aceite refinado de palma hasta un 72% de fracción insaturada (oleína), dependiendo no sólo del sistema de cristalización y las condiciones de tiempo y temperatura, sino del sistema de filtración mecánica usado (Figura 3), filtros con membranas rígidas y flexibles combinadas que permiten obtener los más altos niveles de separación de fases. El proceso de fraccionamiento además de aplicarse en el aceite de palma, también se puede usar para separar las fases saturadas del aceite de pescado y de aceites parcialmente hidrogenados. En el caso del aceite de palma, las fracciones primarias, líquida (oleína) y sólida (estearina), pueden fraccionarse por separado dando lugar a dos nuevos productos, los cuales pueden usarse tanto en la fabricación de helados

con las fracciones intermedias como para la producción de velas ecológicas con las más duras (supe estearinas).

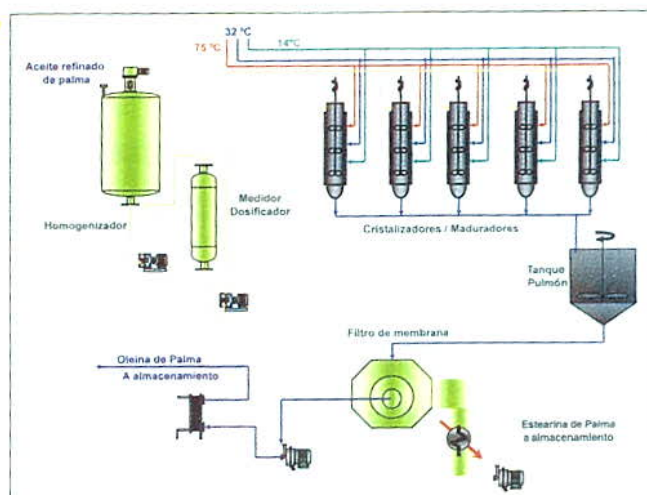


Figura 3. Fraccionamiento en seco de Aceite de Palma.

Interesterificación

La interesterificación es el proceso mediante el cual se logra el intercambio de los ácidos grasos entre los diferentes triacilglicéridos presentes en un aceite o grasa o una mezcla de varios de ellos. Este proceso puede lograrse usando dos diferentes tecnologías, la primera de ellas funciona por vía química, mientras que la segunda se desarrolla por vía enzimática. La interesterificación es un término frecuentemente usado para describir reacciones en las que intercambian los grupos acilo entre un éster y un ácido, *acidólisis*; o un éster con otro éster, *transesterificación* y la de un éster y un alcohol, reacción que se denomina *alcoholólisis* (Perea, 2007).

Existen innumerables aplicaciones de la interesterificación en la industria de alimentos, desde productos de excelente plasticidad para fabricación de tortas, galletas, rellenos y cubiertas hasta lípidos estructurados para alimentación parenteral y potencial en la formulación de alimentos funcionales. Las alternativas de modificación basadas en la interesterificación tienen evidentes diferencias, en especial en la selectividad (los catalizadores enzimáticos actúan selectivamente sobre las posiciones 1,3 de los triacilglicéridos), siendo la interesterificación química regida por la ley de las probabilidades.

También es importante resaltar las diferencias existentes entre los dos procesos de interesterificación, en especial a favor del proceso enzimático, ya que este último se hace a condiciones de baja presión (atmosférica) y temperatura (no mayor de 70°C), no produce residuos peligrosos contaminantes; el aceite o la grasa modificada no requiere blanqueo y rara vez se necesita volver a neutralizar para reducir la acidez al final de la reacción (Figura 4, página 3). Entonces se puede inferir que el proceso de interesterificación tiene hoy unas mayores posibilidades como mecanismo de modificación de grasas, y el método enzimático tendrá seguramente un mayor desarrollo que el método químico ya que incluso se

ha encontrado que los costos (inversión y operación) son ligeramente menores.

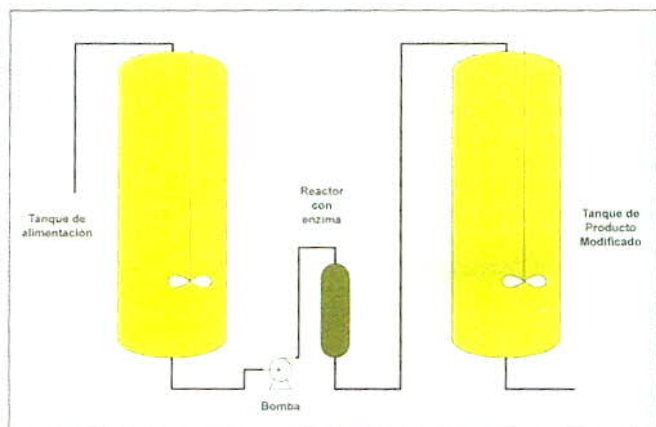


Figura 4. Interesterificación enzimática.

Interesterificación química

La interesterificación química es económica y fácil de escalar y produce grandes cambios en comportamiento cristalino de la grasa y por lo tanto, en sus perfiles de fusión. Sin embargo, la reacción ofrece muy poco o ningún control sobre la distribución de los ácidos grasos en los triacilgliceroles del producto final (Osborn y Akoh, 2002). Este proceso usualmente envuelve la hidrólisis de los triacilgliceroles y reesterificación después de que ha ocurrido una mezcla al azar de los ácidos grasos libres (Akoh 1998; Lee y Akoh, 1998; Osborn y Akoh, 2002).

Industrialmente, se puede realizar calentando el aceite a temperaturas de 200-300°C, pero es un proceso demorado y normalmente acompañado de isomerización, polimerización y descomposición. No obstante, la utilización de compuestos de metales alcalinos y alquilatos de metales alcalinos como catalizadores, permite reducir la temperatura de la reacción a valores entre 50 °C y 100 °C. Los catalizadores más utilizados son los metóxido y etóxido de sodio, seguido del sodio metálico y aleaciones de sodio-potasio, así como los hidróxidos de sodio y potasio en combinación con glicerol (Tabla 1).

Tabla 1. Catalizadores de interesterificación usados en catálisis homogénea.

Catalizadores	(%) (p/paceite)	Temperatura (°C)	Tiempo (minutos)
Alquilatos metálicos (metóxido de sodio)	0.2-2.0	50-120	5-120
Metales alcalinos (Na, K, aleación Na/K)	0.1-1.0	25-270	3-120
Hidróxidos alcalinos + glicerol	0.05-0.1 0.1-0.2	60-160	30-45

El metilato de sodio se utiliza normalmente en proporción de 0,2 a 0,4% con relación al peso del aceite, es altamente reactivo y tóxico, por lo que debe manejarse con cuidado, evitando su contacto con la humedad y el aire. Los hidróxidos son menos reactivos y necesitan temperaturas más elevadas (150°C), pero al igual que los

anteriores catalizadores promueven la migración no controlada y aleatoria de los ácidos grasos en los acilgliceroles, con lo que se pueden generar productos colaterales no deseados, normalmente de difícil remoción (De Greyt *et al.*, 1998; Schuchard *et al.*, 1998; Fenema, 1993; Linden, 1996; D'agostini, 2001).

Las concentraciones del catalizador deben ser bajas para evitar la formación de jabones, y el aceite a ser modificado debe estar seco y bien refinado (bajos índices de acidez, peróxidos y jabones), debido a que el agua, los ácidos grasos libres y los peróxidos actúan como veneno de los catalizadores (De Greyt *et al.*, 1998; D'Agostini, 2001).

Interesterificación enzimática

La interesterificación enzimática se realiza empleando lipasas de origen microbiano. Tiene la ventaja de permitir controlar la distribución de los ácidos grasos sobre la estructura del glicerol, debido a la selectividad y especificidad de estos catalizadores. De esta forma, se pueden fabricar grasas "a la medida" con las propiedades funcionales y nutritivas deseadas, inclusive sintetizar compuestos ópticamente activos para usos químicos y farmacéuticos, entre otras aplicaciones (Schuchardt *et al.*, 1998; Osborn y Akoh, 2002; Xu *et al.*, 2000; Iwasaki y Yamane, 2000).

Adicionalmente, el uso de enzimas evita el empleo de altas temperaturas requeridas por los procesos no enzimáticos, que conducen a la degradación térmica de los productos (p.e., generación de sabores y colores desagradables) y por tanto la necesidad de refinación "aguas abajo" (Paiva *et al.*, 2000).

En comparación con la interesterificación química, los productos interesterificados enzimáticamente no requieren blanqueo ni lavado de la grasa, debido a que no se generan productos colaterales, y al ser las enzimas esteroespecíficas reordenan los ácidos grasos de las posiciones *sn*-1 y *sn*-3 preservando el de la posición *sn*-2, mientras que en el proceso químico las tres posiciones se modifican al azar. Esta especificidad de las lipasas permite obtener una amplia variedad de productos con perfiles de fusión y propiedades nutricionales específicos, así mismo productos novedosos con mejores características sensoriales.

En los procesos enzimáticos, los costos de inversión son menores: requieren únicamente una columna o un tanque, dependiendo si se utiliza un reactor de lecho empacado o un reactor de lote agitado, como equipo especial, por lo que los costos de inversión pueden ser más bajos que los de los procesos de hidrogenación e interesterificación química. Son además procesos ambientalmente limpios debido a que las enzimas no representan un riesgo para el medio ambiente (Volpato, 2003).

Hasta hace poco tiempo, el alto costo de las enzimas era, quizás, el factor más influyente y que limitaba su uso a escala industrial, por lo que en la mayoría de las investigaciones se han evaluado diferentes fuentes de lipasas,

métodos de extracción y purificación e inmovilización en diferentes soportes, con el fin de disminuir el costo de la misma (Akoh, 1998; D'Agostini, 2001). En este sentido, las empresas productoras de enzimas enfocan sus esfuerzos en producir lipasas comerciales de bajo costo que han hecho viables los procesos de interesterificación enzimática.

Las reacciones de interesterificación se pueden realizar en sistemas en discontinuo y en sistemas en continuo. Para la interesterificación enzimática, el principio de los procesos discontinuos es permitir suficiente tiempo de contacto entre el aceite y la enzima para lograr el grado de interesterificación deseado (Novozymes, 2003). Una vez se ha completado la reacción, se suspende el calentamiento y se decanta la mezcla grasa. Se puede cargar nuevamente el reactor con sustrato fresco precalentado para un nuevo reciclo de la enzima. Estos reactores se pueden trabajar con dosis de enzima del 2-10% (p/p) respecto al sustrato, temperaturas alrededor de 40-70 °C en ausencia o presencia de solvente y tiempos de reacción de 2 a 24 horas. Aquí el producto final se separa de la enzima inmovilizada por filtración o decantación (Moreno, 2001; Novozymes, 2001).

Las enzimas inmovilizadas también permiten trabajar en reactores continuos tipo lecho empacado o lecho fijo, con una caída de presión mínima a altas velocidades de flujo (Novozymes, 2003). En estos reactores, el sustrato entra en contacto con una gran cantidad de enzima, por lo que el tiempo de reacción se hace menor comparado con los reactores discontinuos, donde la alta relación sustrato/enzima demanda tiempos de reacción mayores para alcanzar el equilibrio.

Investigadores como Xu *et al.* (1998), Mu *et al.* (1998) evaluaron las reacciones de interesterificación

(acidólisis) en reactores continuos de lecho empacado, con y sin solvente, encontrando que los reactores de lecho fijo son los más promisorios para lograr con éxito la modificación industrial de las grasas catalizada por lipasas, a un precio razonable sobre una base comercial.

Las lipasas como catalizadores

Las lipasas utilizadas en el proceso de interesterificación (triacylglicerol-acilhidrolasas, E.C 3.1.1.3) son enzimas activas en la interfase agua / lípido de las emulsiones. Se pueden emplear en solventes orgánicos y por tanto en química orgánica. Poseen una capacidad intrínseca para romper o hidrolizar enlaces éster en triacylglicerol, diacylglicerol y monoacylglicerol en presencia de un exceso de agua, liberando ácidos carboxílicos y glicerina. En condiciones de bajo contenido de agua (trazas) las lipasas también pueden catalizar la reacción inversa, es decir la esterificación. Además, no necesitan cofactores para su actividad catalítica (Osborn y Akoh, 2002; Koskinen y Klivanov, 1996).

Desde el punto de vista de su especificidad se diferencian las enzimas lipasas que sólo hidrolizan el ácido graso esterificado con los grupos OH primarios del glicerol (*sn*-1,3-específicas), de aquellas que escinden a la misma velocidad los tres enlaces éster (no específicas) (Yamane 1987; Belitz *et al.*, 1997).

Aunque se ha mencionado que la mezcla de varios aceites y grasas no es suficiente para modificar su comportamiento, se usa de manera frecuente de tal manera que se aprovechan las bondades de los aceites que están en mayor proporción en la mezcla y la sinergia de los componentes para satisfacer una necesidad específica.

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Polymorphism of Palm Oil and Palm Oil Products

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Palm oil, palm stearin, hydrogenated palm oil (IV 27.5) and hydrogenated palm olein (IV 28) were crystallized at 5°C, temperature cycled between 5 and 20°C, and kept isothermally at 5°C for 36 days. The polymorphic state of the fats was monitored by X-ray diffraction analysis. Soft laser scanning of X-ray films was used to establish the increase in β crystal content. Palm stearin was least stable in the β' form, followed by palm oil. The hydrogenated oils were very stable in the β' form. Differential scanning calorimeter (DSC) analysis was used to complement the X-ray data.

Palm oil is being used increasingly in foods such as cooking oils, margarines, shortenings and confectionery products. The versatility and adaptability to different food applications of palm oil is the result of its chemical composition. Palm oil differs from many of the common vegetable oils in its high level of palmitic acid, about 44%. In contrast, soybean oil contains 11% and canola oil 5% of palmitic acid. It has been found that addition of palm oil to fats destined for shortening and margarine production has a beneficial effect on their polymorphic stability (1). This stabilizing effect is most likely related to the increased chain length diversity of the fatty acids in these blends. A similar beneficial effect of increased levels of palmitic acid in low erucic acid rapeseed oil obtained by plant breeding has been demonstrated (2).

The incorporation of palmitic acid into the glycerides of a fat should be more effective if the palmitic acid is present mostly in the solid phase of the fat. If this is the case, then the incorporation of suitably modified palm oil might be advantageous. Palm oil is commercially fractionated on a large scale, resulting in a low melting and a high melting fraction known in the trade as palm olein and palm stearin. Palm olein is used as a liquid frying oil; palm stearin can be used as a solid component in margarine and shortening blends (3, 4). Palm oil can also be hydrogenated to yield products with various iodine values and melting points.

This paper deals with the chemical and physical properties of palm oil and modified palm oil and particularly with the polymorphic stability of these fats.

MATERIALS AND METHODS

Refined, bleached and deodorized palm oil, and palm olein and palm stearin were obtained from Palmco Inc., Portland, Oregon. Hydrogenation was carried out in a Parr pressure reaction apparatus with a two-l vessel and a charge of one kg of oil. Nickel catalyst Calsicat E472F (Mallinckrodt Inc., Erie, Pennsylvania) was used at a level of 0.2% by weight of the oil. Reaction temperature was 175°C and hydrogen pressure 103 kPa

(15 psi). Reaction was stopped at IV of about 30. Fatty acid composition of the oils was determined by transesterification and analysis of the methyl esters by gas liquid chromatography (GLC) using a Varian 1400 gas chromatograph with a two-m column packed with 20% DEGS on chromosorb 60-80 mesh operated at 170°C (5).

Iodine value was determined by the Wijs method, AOCS official method Cd 1-25.

Dropping points were determined with the Mettler FP 3 automatic dropping apparatus (6).

Solid fat contents of all fat samples were measured by wide-line nuclear magnetic resonance. A Newport Analyzer Mark III and a sample temperature controller WR 2 MK II were used. Tempering of the samples was done at five temperatures with a Praxis Model TU-900 tempering unit.

Trans isomer content was determined by AOCS method CD 14-61 using a Beckman model 4230 infrared spectrophotometer.

To study the polymorphic stability, 10 g of fat samples in 6-cm long and 10-mm-diameter tubes were cycled as follows: the fat samples were first heated at 70°C for two hr to destroy any "memory" of earlier crystals, then cooled to 5°C and stored at 5°C for one day, followed by three days at 20°C, one day at 5°C, two days at 20°C, one at 5°C, three days at 20°C and, finally one day at 5°C. For constant temperature studies, the tubes were stored at 5°C for up to 36 days.

X-ray diffraction patterns were obtained with a 601 Diffractis X-ray generator and Guinier camera model FR 552 (Enraf Nonius, Delft, The Netherlands), with a temperature controlled sample holder operated at 10°C. Short spacings on the X-ray film were measured with a Guinier viewer and the relative proportions of the β' and β forms established with a Zeinel soft laser scanning densitometer model SLR-504XL interfaced with an Apple IIe computer (Biomed Instruments, Inc., Fullerton, California). The quantitative evaluation was based on the relative densities of the short spacings at 4.6 and 4.2 Å, which are characteristic of the β and β' forms, respectively. The percentage of β crystals was calculated from:

$$\% \beta = \frac{\text{peak area at 4.6 Å}}{\text{peak areas at 4.2 and 4.6 Å}} \times 100$$

At the end of each temperature cycle or storage time, a small sample was taken from the tubes for analysis by DSC with a model 900 DuPont Thermal Analyzer. The samples were heated from 10 to 65°C at 5°C/min.

RESULTS AND DISCUSSION

The properties of palm oil, palm olein, palm stearin, hydrogenated palm oil and hydrogenated palm olein are presented in Table 1. Palm stearin has a higher saturated fatty acid content than palm oil, as evidenced

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TABLE 1

Chemical and Physical Characteristics of Palm Oil, Hydrogenated Palm Oil, Palm Stearin, Palm Olein and Hydrogenated Palm Olein

Fatty acid	Palm oil	Hydrogenated palm oil	Palm stearin fraction	Palm olein fraction	Hydrogenated palm olein
12:0	0.1	—	0.6	0.1	—
14:0	1.0	0.9	1.9	1.0	0.7
16:0	44.7	44.7	60.5	39.6	39.7
18:0	4.0	21.2	4.9	4.0	25.5
18:1	40.1	33.0	26.0	44.0	34.2
18:2	9.5	—	4.8	10.7	—
18:3	0.2	0.2	—	0.5	—
20:0	0.2	—	0.3	—	—
I.V.	51.5	27.5	31.3	57.4	28.0
D.P.	38.6	54.9	53.5	24.4	54.6
% T.I.	0.	12.6	0.	0.	15.7

I.V., Iodine value; D.P., dropping point; T.I., *trans* isomers.

by the higher dropping point and lower iodine value. The chemical composition of hydrogenated palm oil and palm olein were similar. Hydrogenated palm oil contained 12.6% *trans* isomers, hydrogenated palm olein 15.7%. The solid fat contents of the oils are presented in Figure 1. Tables 2 and 3 list the short spacings and their visually estimated intensities. The β' polymorph usually exhibits two strong spacings at 3.8 and 4.2 Å, whereas the β form has one strong spacing at 4.6 Å (7). The β polymorph also shows a weaker spacing at 3.8 Å. For this reason the quantitative evaluation by densitometry involved only the spacings at 4.2 and 4.6 Å. A medium to strong spacing at about 4.3 Å and a weak one at about 4.0 Å may be related to a sub form. Repeated temperature cycling resulted in increased intensity and appearance of the 4.6 Å spacing, indicating a partial transformation to the β form.

An example of a laser densitometer scan of the X-ray films obtained with palm oil at cycle 1 and 4 is

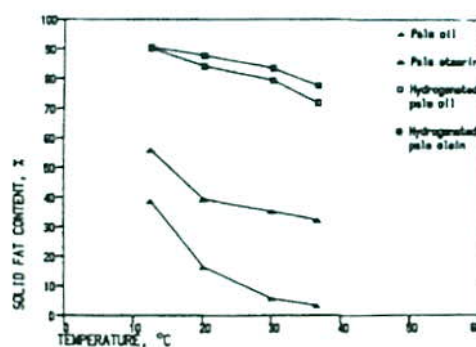


FIG. 1. Solid fat content of palm oil, palm stearin, hydrogenated palm oil and hydrogenated palm olein.

TABLE 2

Short Spacings (Å) of Palm Oil, Palm Stearin, Hydrogenated Palm Oil and Hydrogenated Palm Olein at Different Stages of Temperature Cycling

Cycle ^a	Sample	Form	Short spacings ^{b,c}				
1	Palm oil	β'	—	4.36(s)	4.19(s)	—	3.88(m)
	Palm stearin	$\beta' >> \beta$	4.57(m)	4.35(s)	4.20(s)	4.05(w)	3.87(s)
	Hydrogenated palm oil	β'	—	4.36(m)	4.22(s)	4.06(w)	3.86(s)
	Hydrogenated palm olein	β'	—	4.34(s)	4.19(v.s.)	4.04(m)	3.85(s)
2	Palm oil	β'	—	4.35(m)	4.18(s)	4.04(v.w.)	3.85(m)
	Palm stearin	$\beta' >> \beta$	4.60(m)	4.29(m)	4.20(s)	4.03(w)	3.85(s)
	Hydrogenated palm oil	β'	—	4.33(m)	4.19(v.s.)	4.04(w)	3.83(s)
	Hydrogenated palm olein	β'	—	4.31(s)	4.20(v.s.)	4.03(m)	3.84(s)
3	Palm oil	$\beta' >>> \beta$	4.57(v.w.)	4.35(m)	4.20(s)	4.05(v.w.)	3.87(s)
	Palm stearin	$\beta' >> \beta$	4.56(m)	4.34(m)	4.19(s)	4.00(w)	3.85(s)
	Hydrogenated palm oil	β'	—	4.36(s)	4.22(s)	4.04(w)	3.83(s)
	Hydrogenated palm olein	β'	—	4.31(s)	4.20(v.s.)	4.03(m)	3.84(s)
4	Palm oil	$\beta' >>> \beta$	4.56(w)	4.35(m)	4.19(s)	4.00(v.w.)	3.86(m)
	Palm stearin	$\beta' >> \beta$	4.58(m)	4.35(s)	4.18(s)	4.02(w)	3.85(m)
	Hydrogenated palm oil	β'	—	4.37(m)	4.23(s)	4.02(w)	3.85(m)
	Hydrogenated palm olein	β'	—	4.38(s)	4.22(s)	4.05(m)	3.80(m)

^aCycle 1, 5°C for one day; cycle 2, as in cycle 1 with additional 20°C for 3 days and 5°C for one day; cycle 3, as in cycle 2 with additional 20°C for 2 days and 5°C for one day; cycle 4, as in cycle 3 with additional 20°C for 3 days and 5°C for one day.

^bBand intensities are indicated as v.s., very strong; s, strong; m, medium; w, weak; v.w., very weak.

^cPredominate short spacings of β' , 4.2 and 3.8 Å; β , 4.6 Å.

ACIDOS GRASOS CON ISOMERIA TRANS II. SITUACIÓN DE CONSUMO EN LATINOAMERICA Y ALTERNATIVAS PARA SU SUSTITUCIÓN

ISOMERIC TRANS FATTY ACIDS II. CONSUMPTION IN LATIN AMERICA AND ALTERNATIVES FOR SUBSTITUTION

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ABSTRACT

TFA consumption is well established in developed countries, all of which have begun to adopt policies and regulations to drastically reduce the TFA content of processed foods. Not so in Latin America. We lack up-to-date studies on TFA, and in most cases, have only estimates of TFA consumption based on information from incomplete tables, sometimes from other countries or regions with different consumption habits. Fat intake varies widely within each country or group of countries. Some countries have no regulations governing the fat composition of foods, especially their TFA content. The methodology developed for the industry to reduce the TFA content of hydrogenated products involves the use of oils with high degree of saturation in their natural state, or previously hydrogenated vegetable oils until reaching a high degree of saturation. In light of the nutritional recommendations to reduce TFA intake, it is expected that consumption of these isomers, primarily those of industrial origin, will decrease in the coming years. This paper discusses the sources of the TFA in our diet, the current alternatives for reducing TFA content in foods, and includes information regarding the production and estimated intake of fats and TFA for some Latin American countries for which this information is available.

Key words: *Trans fatty acids, Latin America, alternatives for substitution.*

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INTRODUCCIÓN

El consumo de ácidos grasos con isomería trans (AGT) en los países desarrollados está bien establecido, y prácticamente en todos ellos se han propuesto políticas y regulaciones orientadas a la drástica disminución de la presencia de isómeros trans en los alimentos manufacturados (1). En Latinoamérica la situación es muy diferente. Carecemos de información analítica actualizada, solo son, en la mayoría de los casos, estimaciones de consumo derivadas de información de tablas y estadísticas incompletas o antiguas, y veces de otros países o regiones con hábitos de consumo diferentes. El consumo de materias grasas es muy diverso en cada país o grupo de países. Este consumo está determinado

por la disponibilidad geográfica de materias grasas; en algunos países esta es de origen animal, en otros de origen vegetal, o mezclas de ambos. Además, en varios países hay ausencia de regulaciones sobre la calidad de las materias grasas, y especialmente sobre su contenido de AGT.

En este trabajo se discuten las alternativas actualmente disponibles para reducir el contenido de AGT en los alimentos. Además, analiza cual es la situación en algunos países de la Región Latinoamericana, de los cuales se dispone información respecto al consumo de AGT y su regulación. Finalmente propone acciones orientadas a disminuir sustancialmente el consumo de AGT en los diferentes países de Latinoamérica.

COMO REDUCIR EL CONSUMO DE ACIDOS GRASOS TRANS

En consideración a las recomendaciones nutricionales que sugieren reducir el consumo de AGT, se espera que la ingesta de estos isómeros, principalmente los de origen industrial, disminuya en los próximos años. En la actualidad la reducción se ha producido, principalmente, por la introducción al mercado mundial de margarinas y mantecas libres de trans, identificadas como productos "VTF" (*virtually trans free*), las que ya se comercializan en varios países de Latinoamérica. Es importante mencionar que el desarrollo de este tipo de margarinas fue la respuesta por parte de la industria de alimentos a la creciente presión ejercida por la comunidad científica, que demostró con evidencias experimentales, clínicas, y epidemiológicas, que el consumo de AGT afecta negativamente la salud cardiovascular (2).

La metodología desarrollada para reducir el contenido de AGT en los productos hidrogenados se basa en el uso de aceites con alto grado de saturación en forma natural (como el aceite de palma o palmiste), o de aceites vegetales (soja, girasol, algodón, maíz, entre otros) previamente hidrogenados hasta alcanzar un alto grado de saturación (full hidrogenación). En ambos casos, el nivel de AGT es mínimo o inexistente. Estos aceites se

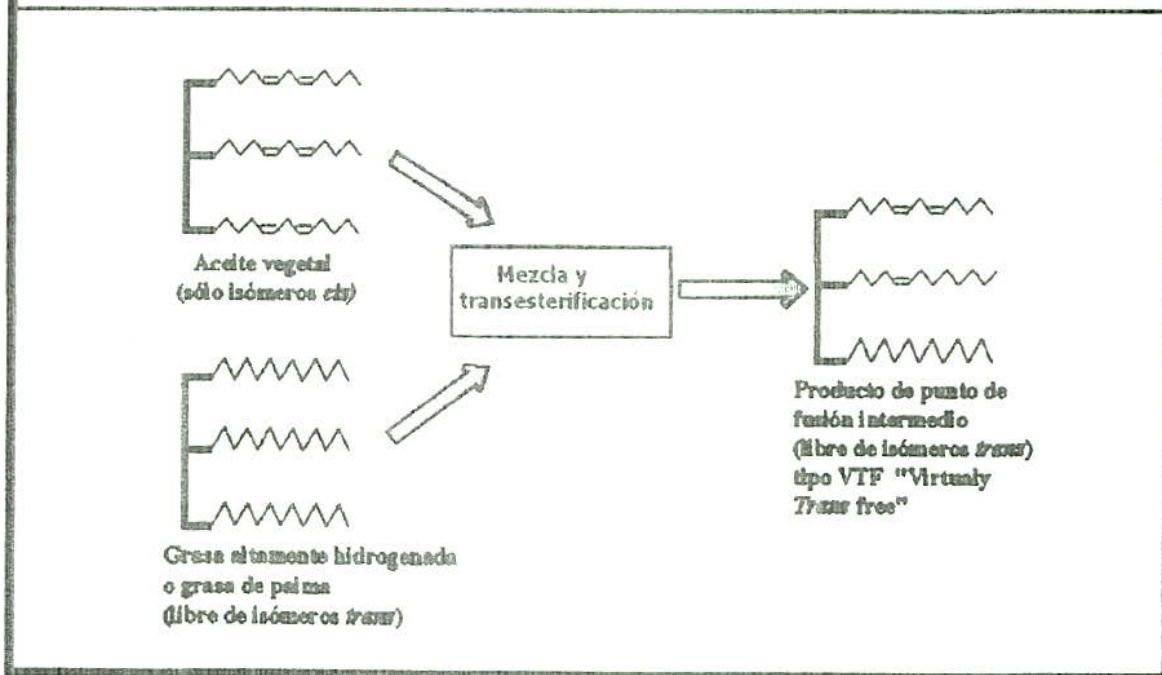
mezclan con aceites vegetales refinados relativamente insaturados (girasol, soja, maíz, entre otros) que también poseen en su origen cantidades mínimas de AGT (3). La mezcla se somete a un proceso de transesterificación (4) que consiste en el intercambio de ácidos grasos entre los triacilglicéridos que forman ambos tipos de aceites (altamente hidrogenados y no hidrogenados) (5).

Este proceso se puede realizar en forma química, o enzimática. El proceso químico es de menor costo pero produce mezclas de triacilglicéridos de composición variable, ya que es un proceso de intercambio de ácidos grasos al azar. El procedimiento enzimático, que es el que se está imponiendo en los países desarrollados, es de mayor costo pero permite obtener productos con una composición y propiedades muy específicas y de acuerdo al requerimiento del productor (6). La figura 1 esquematiza el procedimiento para la obtención de margarinas del tipo VTF mediante la transesterificación de aceites hidrogenados y no hidrogenados.

El contenido de AGT en las margarinas es actualmente informado obligatoriamente en el etiquetado nutricional de estos productos en muchos países, pero el aporte de AGT en productos elaborados con aceites parcialmente hidrogenados, como es el caso de productos para panificación, galletas, galletitas, cereales, bocadi-

FIGURA 1

Como se puede obtener productos hidrogenados libres de ácidos grasos trans



llos, papas fritas, entre otros, no es siempre informado, y en algunos casos este contenido "oculto" es considerablemente elevado, e incluso mayor al aportado por las margarinas y mantecas que no son VTF. Al respecto, la FDA de Estados Unidos determinó que el contenido de AGT debe ser indicado en todos los etiquetados nutricionales de los alimentos elaborados con aceites parcialmente hidrogenados, a partir de 1° de enero del año 2006. En Latinoamérica esta información ya es obligatoria en algunos países en el etiquetado nutricional de los alimentos que contienen un cierto porcentaje de materias grasas, aunque la situación es muy dispar, como se analiza en la siguiente sección.

Un aspecto que es motivo de discusión actualmente, se refiere a que los procesos de reducción de AGT a través de los procesos de hidrogenación y transesterificación, si bien implican una reducción sustancial de los AGT, también producen un aumento del contenido de ácidos grasos saturados, los que son tanto o más dañinos para la salud que los AGT. En los productos tipo margarinas o mantecas esto es, al menos por ahora, inevitable, de modo que se debe ponderar el costo/beneficio en el impacto de salud que pueda producir esta transformación tecnológica. Sin embargo, en los aceites utilizados para procesos de fritura tanto industrial como doméstica, hay notables progresos. Algunos de ellos se describen a continuación.

Como alternativa a la transesterificación se ha modificado, por selección o modificación genética, la composición de algunos aceites de producción y comercialización masiva, como lo son el aceite de soja, de girasol, etc, obteniéndose aceites libres de AGT y de gran estabilidad térmica. Estos aceites son muy adecuados para ser utilizados en procesos de fritura y/o de horneado industrial y doméstico. Es el caso del aceite de soja de alta concentración de ácido oleico y baja concentración de ácido linolénico (Mid-Oleic/Low-Linolenic SBO), el aceite de soja de bajo contenido de ácido linolénico (Low-Linolenic SBO), el aceite de soja de mínimo contenido de ácido linolénico (Ultra Low-Linolenic SBO), el aceite de girasol de mayor contenido de ácido oleico (Mid-Oleic SFO), el aceite de girasol de alto contenido de ácido oleico (High-Oleic SFO), fracciones de aceite de palma y palmiste de bajo contenido de ácidos grasos saturados, entre otros. Recientemente se desarrolló un aceite de girasol con alta concentración de ácido esteárico, un producto que se beneficiaría del efecto "neutro" de este ácido graso en el perfil lipídico (7). La industria oleoquímica ofrece hoy día, procesos y una amplia variedad de productos, para el desarrollo de materias grasas con bajo contenido de AGT y para la manufactura de alimentos con mínimo contenido de AGT.

En algunos países de Latinoamérica es frecuente el uso de aceite de palma en la fabricación de margarinas. El aceite de palma, en su composición original, no tiene efectos negativos en el perfil lipoproteico y del colesterol, debido a la distribución de los ácidos grasos en los triglicéridos que lo forman (8, 9). El ácido palmítico (P), que es el ácido graso mayoritario en el aceite de palma (80%), ocupa principalmente las posiciones 1 y 3 de los triacilglicéridos. La posición 2 es ocupada por ácido oleico (O) y linoleico (L). De esta forma el triacilglicérido mayoritario en el aceite de palma es Palmítico-Oleico-Palmítico (POP) y en menor proporción Palmítico-Linoleico-Palmítico (PLP). Los ácidos grasos saturados C16 o mayores que ocupan las posiciones 1 y 3 de los triacilglicéridos, presentan baja absorción intestinal, por lo cual son considerados como "neutros" (10, 11). Es el caso del ácido esteárico en las grasas de origen animal y del ácido palmítico en el aceite de palma. Cuando este aceite se utiliza para la fabricación de margarinas, el proceso de transesterificación modifica la estructura original Palmítico-Oleico-Palmítico (POP) y Palmítico-Linoleico-Palmítico (PLP), generando mezclas al azar de triacilglicéridos, con lo cual se pierde el efecto "neutro" del ácido palmítico, el cual pasa a comportarse como un típico ácido graso saturado. Es importante tener en cuenta este aspecto cuando se considera al aceite de palma como una alternativa para la producción de margarinas libres de AGT, ya que debido a la transesterificación a que se somete, su consumo puede afectar negativamente el perfil lipídico.

CONSUMO DE AGT EN LATINOAMERICA, LA SITUACIÓN EN ALGUNOS PAISES

La estimación del consumo de AGT siempre es controversial, ya que los cálculos varían según el método utilizado: cuestionarios de ingesta de alimentos, información sobre disponibilidad o consumo de alimentos, extrapolaciones derivadas del contenido de AGT en el tejido adiposo o en la leche derivadas de ecuaciones teóricas de la literatura, disponibilidad de tablas de contenido de AGT de diversos alimentos (las que mayoritariamente no están disponibles en Latinoamérica), o en el mejor de los casos, de análisis específicos del contenido de AGT de los alimentos consumidos por una población específica (1, 12).

Las principales fuentes dietarias de AGT son las margarinas, mantecas, y las grasas industriales utilizadas en la elaboración de productos de repostería, panificación, bocadillos, entre otros, las que constituyen la llamada grasa "oculta" o "invisible", que contiene aceites vegetales y/o marinos parcialmente hidrogenados, y cuyos orígenes son muy diferentes en cada

país, y difíciles de evaluar y cuantificar. Se han hecho diversas estimaciones sobre el consumo de AGT. Por ejemplo, en Estados Unidos la estimación ha sido de 7,6 a 8,1 g/d (13), e incluso se ha llegado a reportar un consumo de aproximadamente 14 g/d al considerar que las grasas de uso industrial tienen hasta un 30% de AGT, y que algunas margarinas pueden tener cantidades superiores al 40% de AGT (14). En otros países, como Alemania e Inglaterra, el consumo es menor (4,9-6,6 g/d) (15), y además, este consumo está determinado en un alto porcentaje (35%) por AGT derivados de carnes y lácteos provenientes de animales rumiantes (16). Sin embargo, en países de menor desarrollo, como India, se ha estimado un consumo promedio mucho menor, el que no supera a los 3g/d (16).

En el caso de Latinoamérica, la información es muy parcial, ya que en la mayoría de estos países no existe una evaluación sistematizada del consumo de AGT de diferente origen. Además, en muchos de estos países no se cuenta con la tecnología para la adecuada determinación analítica de estos isómeros, o si existe, pertenece a entidades, generalmente industrias, que utilizan la información solo con fines internos. Otro aspecto que complica la información, es que por razones geográficas y de producción agrícola, y marina en algunos casos, muchos países disponen de diferentes fuentes de materias grasas, las que se utilizan en algunos y no en otros, por razones principalmente económicas.

En el mes de abril de 2007, con el auspicio de la Organización Panamericana de la Salud, se realizó en la ciudad de Washington DC, Estados Unidos, una reunión de especialistas estadounidenses, canadienses y latinoamericanos, para analizar y discutir políticas tendientes a disminuir el consumo de AGT en Latinoamérica. Esta iniciativa, bajo el lema "Latinoamérica libre de grasas trans" tuvo una importante repercusión ya que en varios países de la Región se iniciaron acciones concretas para cumplir con este cometido. Al autor se le encomendó realizar una investigación sobre la situación latinoamericana del consumo de AGT. A continuación se presenta una compilación de datos correspondiente a dicha investigación respecto de la producción y el consumo estimado de materias grasas y de AGT en algunos países latinoamericanos, desde los cuales fue posible obtener información.

Argentina

Argentina es el segundo mayor productor y el primer exportador de oleaginosas (semillas y aceites) de Latinoamérica, siendo el aceite de girasol, el aceite de soja, y el aceite de oliva sus principales productos. También produce una importante cantidad de sebo vacuno, el que

es utilizado en la fabricación de margarinas y mantecas industriales. Existe una pequeña producción de aceite de pescado y de calamar, principalmente para usos industriales, y minoritariamente para hidrogenación. La disponibilidad de materias grasas per cápita/día fue de 106,1 g, lo que equivale a 36,9 Kg/año (2002). El 61% de esta disponibilidad es grasa de origen animal y el 39% de origen vegetal. Argentina es el mayor consumidor de carne vacuna de la región. Un 45% de la producción de materias grasas se exporta a diversos países del mundo en la forma de sebo, aceites crudos y aceites refinados, por lo cual el consumo real sería de 58,3 gr per cápita/día, lo que equivale a 21,3 Kg/año. Las margarinas y mantecas se preparan a partir de sebo vacuno y en menor proporción a partir de aceites vegetales hidrogenados.

La declaración del contenido de AGT en productos que contienen materias grasas es obligatoria a partir de 2006, aunque no hay estimación del consumo por parte de la población. Existen estudios sobre el contenido de AGT en productos de alto consumo, como las galletitas (8,9 Kg/mes por hogar), las que contienen 3 a 13% de AGT. En los últimos años se ha producido un fuerte aumento del consumo de aceite de girasol alto oleico. Numerosos productos declaran ser "libres de trans", todos de origen nacional. Existe capacidad analítica para la determinación de AGT en entidades académicas, reguladoras, y en la industria. La difusión de información sobre los efectos del consumo de materias grasas sobre la salud es liderada por PROPIA (Programa de Prevención del Infarto en Argentina), a través de campañas de comunicación, congresos, talleres, entre otros. PROPIA lidera, además, el proyecto "Grasas buenas para Latinoamérica". ASAGA (Asociación Argentina de Grasas y Aceites) es una importante entidad gremial y académica, filial de AOCS (*American Oil Chemist's Society*) que realiza difusión técnica sobre materias grasas, pero con poca participación en temas de salud asociados al consumo de AGT. ASAGA publica en forma bimensual la revista Aceites y Grasas, de amplia difusión en Latinoamérica.

Fuente de información: Lic. Lorena Lazo (PROPIA), Hojas de Balance de FAO 2002, Secretaría de Agricultura, Ganadería, Pesca y Alimentos de Argentina.

Brasil

Brasil es el primer productor de oleaginosas de Latinoamérica y el sexto en el mundo. El principal producto es el aceite de soja (90%), seguido del aceite de algodón (4%), y de palma (2%). Existe producción y consumo de sebo animal, aunque no hay disponibilidad de información. El consumo de materias grasas per cápita/día fue de 27,9 g, lo que equivale a 10,18 Kg/año (2003). Tanto

la cantidad, como la proporción de materias grasas consumidas, varía notablemente en las diferentes regiones del país, siendo la región centro-oeste la que presenta el mayor consumo de materias grasas (35,15 g/día) y la región del noreste el menor consumo (22,1 g/día). El 76% corresponde a grasas de origen vegetal y el 24% a grasas de origen animal. Los productos hidrogenados se preparan principalmente a partir de aceite de soja. La declaración del contenido de AGT es obligatoria en los productos que contienen materias grasas, aunque no hay estimaciones del consumo por parte de la población. Existen estudios sobre el contenido de AGT en productos de alto consumo (bollos, viscochos, roscas, helados, margarinas vegetales, entre otros) los que contienen 2,2-4,5 g/100 g de AGT. Existe una gran cantidad de productos que declaran ser "libres de trans", todos de origen nacional.

Existe capacidad analítica para la determinación de AGT en instituciones académicas, institutos de investigación, y organismos públicos reguladores. Existe una amplia difusión sobre el contenido y los efectos en la salud de los AGT en revistas de alta circulación, periódicos, programas radiales y de televisión. Oleos e Gorduras de Brasil es la filial de AOCS. Realiza difusión sobre aspectos técnicos de materias grasas, aunque aborda pocos temas de salud asociados al consumo de AGT.

Fuente de información: Dra Ana Beatriz Vasconcellos, Coordinadora General de Políticas de Alimentación y Nutrición, Ministerio de Salud, Brasil. Dr. Jorge Mancini, Profesor de la Universidad de Sao Paulo. Dr. Daniel Barrera, Profesor de UNICAMP, Presidente de Oleos y Gorduras de Brasil.

Chile

Chile no es un productor de materias grasas como materia prima para consumo humano, por lo cual no se autoabastece. El 95% de los aceites, principalmente soja/girasol (generalmente mezcla 80%:20%), se importan desde Argentina, y en un porcentaje menor desde Bolivia. Un 50% se importa refinado y listo para el consumo y un 50% se refina en las seis plantas de refinación industrial actualmente en operación. Existe una limitada producción de raps modificado (canola) (5-5,5%), cuyo consumo va destinado principalmente a la industria salmonera, como sustituto del aceite de pescado, muy escaso y de muy alto precio en la actualidad (US 1.600-1.800/T). Existe una pequeña producción de aceite de pepita de uva (0,8-1%) y de maíz (1%). Se produce aceite de oliva virgen y extravirgen (2,3%) de muy buena calidad, pero que no representa más del 1% del consumo.

El consumo de materias grasas per cápita fue de 29,2 g/día, lo que equivale a 10,7 Kg/año (2003). La hidrogenación industrial se realiza a partir de aceite

de soja, girasol, o de mezclas de ambos. Un 30% de la hidrogenación está destinada a la fabricación de margarinas de mesa, las que en un 90% cumplen con el descriptor de "libre de trans" (menos de 0,5 g de AGT por porción), cuya declaración es obligatoria en el etiquetado nutricional desde el mes de noviembre de 2006. El 70% restante de los productos de hidrogenación industrial se obtienen utilizando aceite de salmón (de alta disponibilidad) o mezclas de aceite de salmón y soja, o sebo animal que se importa desde Argentina. Estas grasas hidrogenadas son para uso industrial (grasa invisible) y no están reguladas en la declaración de su composición. Dependiendo de las materias primas de origen y del grado de hidrogenación, pueden contener hasta un 40-45% de AGT. No existe estimación del consumo de AGT, pero hay estudios sobre el consumo a partir de papas fritas y bocadillos.

La cuantificación de AGT se realiza en instituciones académicas, de investigación, laboratorios privados, y en industrias. Las cadenas de comida rápida han comenzado a incorporar en sus procesos de fritura "en el local" aceites de alta estabilidad térmica, como lo es el girasol alto oleico (en Chile, maravilla alto oleico.), pero la fritura industrial sigue utilizando materias grasas parcialmente hidrogenadas cuya composición de AGT es variable, ya que con frecuencia se modifica la composición de acuerdo a la disponibilidad de materias primas y precio del momento.

Las autoridades de salud han alertado sobre el riesgo del consumo de AGT y orientan a consumir productos con cantidad reducida de AGT. Las organizaciones de consumidores, permanentemente monitorean la rotulación de las materias grasas, alertando sobre posible rotulación engañosa de margarinas y mantecas, pero tienen poco impacto en el consumidor. Con frecuencia se informa sobre los riesgos para la salud derivados de los AGT en la prensa y en revistas de alta circulación. Esporádicamente se comenta en programas de radio y TV. La Corporación Chilena de Grasas y Aceites (CORCHIGA) es una filial de AOCS, agrupa a las principales empresas relacionadas con la manufactura y procesamiento de materias grasas. Su nivel de influencia en los organismos reguladores y de comunicación es muy limitado.

Fuente de información: Ing. Fernando de la Barra (Especialidades Industriales), CORCHIGA, Dr. Alfonso Valenzuela, INTA, Universidad de Chile.

Costa Rica

Costa Rica produce aceite de soja, girasol y maíz, los cuales representan el 95% del consumo de materias grasas vegetales. No se cuenta con información sobre el consumo de materias grasas de origen animal, el que

es pequeño. Los productos hidrogenados que utiliza la industria de alimentos son mayoritariamente importados de los Estados Unidos. El consumo de materias grasas per cápita es de 36,7 g/día y el consumo de AGT se estima en 2,6 g/día. Existen productos que incluyen el contenido de AGT en su etiquetado, pero esta declaración no es obligatoria. Hay estudios sobre el consumo de AGT por parte de la población y tablas de alimentos que incorporan el contenido de AGT.

Fuente de información: Dr. Rafael Monge, Instituto Costarricense de Investigación y Enseñanza en Nutrición y Salud (INCIENSA).

Colombia

Colombia es un importante productor de aceite de palma y palmiste, principal materia grasa de consumo habitual. También produce aceite de soja. Hay una oferta limitada de aceite de girasol de producción nacional y también de importación. La industria utiliza grasa bovina y porcina como materia prima para la manufactura de alimentos. El consumo de materias grasas se calcula en 63 g/día. No existen estimaciones sobre el consumo de AGT y no hay reglamentación al respecto, por lo cual no es obligatoria la declaración de contenido de AGT. Tampoco existen estudios al respecto.

Fuente de información: nutricionista Sylvana Dandan, Universidad del Bosque y FEDEPALMA.

Perú

El Perú produce aceite de soja, de algodón y de girasol, que son las principales fuentes de consumo de materias grasas. Además, es un importante productor de aceite de pescado, que se hidrogena para utilizarlo en la fabricación de margarinas y mantecas. El consumo de materias grasas se estima en 29,5 g/día, y el consumo de AGT es de 2,0 g/día. No es obligatoria la declaración del contenido de AGT en los alimentos, y existen estudios sobre el consumo de AGT presentes en algunos productos. La cuantificación de AGT se realiza en laboratorios privados y en el Instituto de Investigaciones Pesqueras, en Callao.

Fuente de información: nutricionista Milagros Agurto, Universidad Científica del Sur.

Puerto Rico

Puerto Rico no es productor de materias grasas, y su consumo de estas sustancias proviene en su totalidad de productos importados de los Estados Unidos, dada su condición de Estado Libre Asociado. Los aceites de mayor consumo son los de soja, maíz y canola. La grasa de origen animal es principalmente porcina y los productos hidrogenados provienen del sebo bovino y de aceites vegetales. El consumo de materias grasas per

cápita es de 80-100 g/día. No hay estimaciones sobre el consumo de AGT. La declaración del contenido de AGT es obligatoria, en consonancia con la reglamentación de los Estados Unidos, de donde provienen la totalidad de los productos que los contienen. No hay estudios sobre el contenido de AGT de los productos de consumo habitual, aunque este es deducible del etiquetado nutricional de los productos.

Fuente de información: Dr. Waldert Rivera, Departamento de Salud, Ministerio de Salud, Puerto Rico.

Uruguay

Uruguay consume principalmente aceite de girasol, de arroz, y soja. El 62% es de origen nacional y el 38% se importa desde Argentina, principalmente aceite de soja. El consumo estimado de materias grasas per cápita es de 44 g/día, lo que equivale a 16,1 Kg/año. Las margarinas que se consumen son mayoritariamente importadas de Argentina e incorporan el etiquetado de origen. No se tiene información sobre el consumo de AGT, aunque es obligatoria la información de su contenido en los alimentos. Se han realizado estudios sobre el contenido de AGT en diferentes alimentos de gran consumo. La determinación del contenido de AGT se realiza solamente en los Laboratorios de la Facultad de Química de la Universidad de la República. La comunicación sobre los efectos de los AGT en la salud es escasa, solo en medios escritos y radiales. La Comisión Honoraria para la Salud Cardiovascular se ha preocupado de realizar actividades de divulgación a médicos y nutricionistas sobre los efectos de los AGT.

Fuente de información: Dra María Antonia Grompone, Facultad de Química, Universidad de la República.

Venezuela

Venezuela consume aceite de maíz, de girasol, de soja, canola, y de maní, en menor escala. Las margarinas son en su mayoría importadas, aunque se utiliza aceite de palma para la fabricación de margarinas de origen nacional. El consumo de materias grasas per cápita es de 70 g/día, lo cual equivale a 25,6 Kg/año (1999). No existen antecedentes sobre el consumo de AGT y no es obligatoria la declaración de contenido de materias grasas en los alimentos. Solo los productos importados, mayoritariamente de Estados Unidos, declaran AGT en sus etiquetas. Solo una entidad académica posee tecnología para la determinación de AGT. No hay estudios de contenido de AGT en alimentos de gran consumo. No existe divulgación sobre AGT en medios escritos o visuales. ASOAGRA es la filial venezolana de AOCS, pero tiene escasa muy escasa actividad de información y divulgación.

Fuente de información: Dr. Virgilio Bosch. Sección Lipodología, Instituto de Medicina Experimental, Universidad Central. Ing. Morelia González, Secretaría Ejecutiva de ASOAGRA.

La figura 2 resume la información obtenida desde los diferentes países de la Región.

CONCLUSIONES Y RECOMENDACIONES

La conclusión general es que los AGT afectan negativamente la salud cardiovascular y su consumo constituye un riesgo potencial para aumentar la incidencia de esta patología, que es la primera causa de muerte en el mundo occidental y en Latinoamérica. Recientemente el Comité de Nutrición de la *American Heart Association* (AHA) elaboró una detallada revisión sobre "Recomendaciones de Estilos de Vida, 2006" (17), en las que recomienda, entre otras cosas, un consumo de grasas saturadas menor al 7% de la energía (anteriormente se recomendaba menos del 10%). Recomienda, además, una sustitución del consumo de grasas hidrogenadas por aceites líquidos, enfatizando la excepción de los aceites tropicales (palma y palmiste, en el caso de Latinoamérica), aunque de acuerdo a lo comentado en el párrafo anterior, podría ser discutible. Aunque en la

actualidad no hay recomendaciones de cantidad máxima de ingesta de AGT, el Comité de la AHA valida las recomendaciones del Comité de Nutrición de la FDA, en el sentido de reducir al máximo la ingesta de AGT, siendo deseable un consumo igual o menor al 1% de la energía. Se espera que la obligatoriedad de informar el contenido de AGT en el etiquetado nutricional de muchos productos que contienen materias grasas, oriente al consumidor y produzca un cambio en sus hábitos de consumo respecto a los AGT.

A la luz de los resultados obtenidos a partir de numerosos protocolos experimentales, de diferente diseño y criterios de evaluación de los resultados, y de las recomendaciones de diferentes Comités de Salud y Nutrición, es posible establecer como conclusión que los AGT, provenientes de aceites vegetales y/o marinos parcialmente hidrogenados, modifican negativamente los niveles de los lípidos plasmáticos, aumentando significativamente el riesgo de enfermedad cardiovascular y potencialmente el de otras enfermedades, aunque para estas últimas aún no se cuenta con la evidencia definitiva. De esta conclusión general, se derivan, como propuesta del autor, las siguientes recomendaciones orientadas a los Organismos Reguladores de los distin-

FIGURA 2							
Consumo de mateias grasas en latinoamérica (situación de algunos países)							
	ACEITES COMESTIBLES	GRASAS COMESTIBLES	PRODUCTOS HIDROGEN.	CONSUMO MAT. GRASAS (g/día)	CONS. EST. AGT (g/día)	DECLARACION EN ETIQUETADO	ESTUDIO SOBRE CONT./CONS. AGT
ARGENTINA	GIRASOL (N) SOJA (N) OLIVA (N)	BOVINA (N)	VEGETAL SEBO	106.2	7.2	SI	SI, EN VARIOS ALIMENTOS
BRASIL	SOJA (N) ALGODÓN (N) PALMA (N, I)	BOVINA (N)	VEGETAL	27.9	ND	SI	SI, EN VARIOS ALIMENTOS
CHILE	GIRASOL (I) SOJA (I) OLIVA (N, I) MAIZ (I)	BOVINA (N, I) PORCINA (N)	VEGETAL PESCADO SEBO	29.2	4.5	SI	SI, EN VARIOS ALIMENTOS
COLOMBIA	PALMA (N) SOJA (N) GIRASOL (N, I)	BOVINA (N) PORCINA (N)	VEGETAL SEBO	63	ND	NO, EN TRAMITE	ND
COSTA RICA	SOJA (N) GIRASOL (N) MAIZ (N)	ND	VEGETAL	36.7	2.5	SI, NO OBLIGATORIA	SI, TABLA DE COMPOSICION
PERU	SOJA (N) ALGODÓN (N) GIRASOL (N)	BOVINA (N)	VEGETAL PESCADO	29.5	2.5	NO	SI, MUY RESTRINGIDOS
PUERTO RICO	MAIZ (I) SOJA (I) CANOLA (I)	PORCINA (I)	VEGETAL SEBO	80-100	ESPECIFICADO POR PRODUCTO	SI (I)	ND
URUGUAY	GIRASOL (N, I) SOJA (N, I) ARROZ (N)	BOVINA (N)	VEGETAL SEBO	64	ND	SI	SI, EN VARIOS ALIMENTOS
VENEZUELA	GIRASOL (N) SOJA (N) CANOLA (N, I) MANI (N)	ND	ND	70	ND	NO, SALVO IMPORTADOS	ND

(N): PRODUCTO NACIONAL
(I): PRODUCTO IMPORTADO
ND: NO DISPONIBLE

tos Gobiernos de la Región, a la Industria de materias grasas y de alimentos en general, a las Organizaciones gubernamentales y/o privadas que velan por la salud y nutrición de la población, a los medios de comunicación, y al público consumidor en general.

Organismos Reguladores

Perfeccionar, o elaborar, cuando no existan, el o los marcos regulatorios sobre la producción, manejo y consumo de materias grasas, con especial énfasis en la obligatoriedad del etiquetado nutricional de los alimentos, el cual debe incorporar la declaración del contenido de AGT cuando corresponda.

Definir el uso de los descriptores "reducido en AGT", "bajo en AGT" y "libre de AGT", según corresponda, identificando el tipo de productos, según su contenido, en los cuales se puedan aplicar estos descriptores.

Regular la identificación y rotulación de la grasa "oculta o invisible" contenida en muchos alimentos, ya que constituye una fuente importante de AGT en la alimentación latinoamericana.

Realizar los máximos esfuerzos para dar a conocer al público consumidor el riesgo del consumo de AGT, sensibilizando sobre el efecto negativo que estos tienen en la salud.

Industria de materias grasas y alimentos en general

Se debe estimular a la industria de alimentos para que reduzca, en lo posible, la presencia de AGT en los productos de consumo masivo. Se debe incentivar la incorporación de procesos tecnológicos que eliminan la formación de AGT, y/o el reemplazo por materias grasas alternativas. No se deben utilizar mensajes publicitarios, tales como «bajo en ácidos grasos saturados», cuando un producto es rico en AGT contenidos entre los ácidos grasos insaturados, pero no informados, o incluidos entre los ácidos grasos insaturados.

La industria de alimentación institucional y las cadenas de comida rápida, deben reducir y eventualmente eliminar, en plazos establecidos, el uso de materias grasas parcialmente hidrogenadas e hidrogenadas, en todas sus líneas de procesos, reemplazándolas por productos con bajo o mínimo contenido de AGT. En los procesos de fritura tanto industrial como en locales de expendio, se deben utilizar aceites líquidos de alta resistencia térmica en reemplazo de los productos hidrogenados.

Organizaciones gubernamentales y privadas que velan por la salud de la población

Desarrollar programas de información y de difusión, a través de los medios de comunicación y de divulgación,

sobre los riesgos de salud derivados del consumo de los AGT y de las materias grasas hidrogenadas en general. Incentivar la organización de paneles, cursos, talleres, entre otros, a los profesionales de la salud, de la nutrición, de la educación, y de la industria, en los cuales se de a conocer el riesgo del consumo de los AGT

Estimular la instalación de laboratorios de análisis cuantitativo de AGT, que presten apoyo y asesoría a la industria, a los organismos reguladores, de comunicación, y al público en general. Facilitar el desarrollo de Laboratorios de Referencia a nivel nacional o regional con el objetivo de estandarizar procedimientos analíticos y de capacitar personal.

Público consumidor

Informar y orientar sobre el riesgo de salud de los AGT, estimulando la elección de aquellos productos que no los contienen. Deben iniciarse campañas de comunicación y educativas, dirigidas al público consumidor, en general, orientadas a informarlo sobre qué son los AGT, cuales son sus efectos en la salud, donde están contenidos, como seleccionar las materias grasas de su consumo, a aprender a leer el rotulado nutricional de los productos que adquiere, y a exigir la debida información en aquellos productos que incorporan la información.

Se espera que en los próximos años disminuya sustancialmente el consumo de AGT en la dieta latinoamericana debido a las presiones ejercidas por los organismos que agrupan a los consumidores, a las regulaciones establecidas por la entidades pertinentes, y a la propia respuesta de la industria de manufactura de materias grasas, que ya ha logrado en algunos países reducir sustancialmente la aplicación de los procesos de hidrogenación, beneficiándonos con productos virtualmente libres de AGT. Las empresas de alimentación y de comida rápida, cuyas casas matrices se encuentran principalmente en Estados Unidos, también se han unido a esta iniciativa. En una comunicación reciente del CSPI (*Center for Science in the Public Interest*) del 29 de diciembre, 2006, se informa que las principales cadenas de comida rápida han iniciado una drástica reducción del contenido de AGT de sus productos en Estados Unidos, por lo cual se espera que el bienio 2008-2009 "sea el año de la virtual eliminación de los isómeros *trans* de origen tecnológico". Finalmente, se espera que las iniciativas de estas empresas también sean efectivas en sus respectivas representaciones en los distintos países de Latinoamérica. Se deben realizar los máximos esfuerzos individuales y colectivos en los diferentes países para lograr que Latinoamérica pueda ser declarada una Región libre de AGT.

RESUMEN

El consumo de AGT está bien establecido en los países desarrollados, en los que se han elaborado políticas y regulaciones para reducir drásticamente su contenido en los alimentos procesados. No ocurre lo mismo en Latinoamérica. Son escasos los estudios sobre consumo de AGT y en la mayoría de los casos son solo estimaciones basadas en información incompleta, a veces procedente de otras regiones o países con hábitos de consumo diferentes. El consumo de grasas varía mucho de un país a otro, e incluso dentro de un mismo país. Algunos países no tienen regulaciones sobre el consumo de grasas y el contenido de AGT de los alimentos. **La metodología desarrollada por la industria para reducir el contenido de AGT de los productos hidrogenados, involucra el uso de aceites con alto grado de saturación en su condición natural, o el uso de aceites vegetales con un alto grado de hidrogenación previa. Se espera, en vista de las recomendaciones nutricionales, que el consumo de AGT, principalmente aquellos de origen industrial, se reduzca considerablemente en los próximos años. Este trabajo discute las fuentes de AGT en nuestra dieta, las alternativas para reducir el consumo de AGT en los alimentos, e incluye información sobre la producción y el consumo estimado de AGT de algunos países de Latinoamérica de los cuales se dispone de información.**

Palabras claves: Ácidos grasos trans en Latinoamérica, alternativas de sustitución.

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Fraccionamiento en seco de los aceites de palma y de palmiste y usos de las fracciones

Dry Fractionation of Palm and Kernel Oils and Fraction Uses

Antonio E. Cadena G.¹

Resumen

A pesar de que desde los comienzos de la segunda mitad del siglo XIX ya se practicaba el fraccionamiento del sebo para obtener la "oleomargarina", y que en 1921 se patentó un proceso semicontinuo para separar los aceites de las estearinas usando separadoras centrífugas, el fraccionamiento de aceites y grasas sólo empezó a tener importancia industrial después de 1950 y especialmente a partir de 1970, gracias al auge en el cultivo de palma de aceite en países como Malasia e Indonesia. Los desarrollos que se han dado en otros sectores industriales, así como el advenimiento de técnicas analíticas como la cromatografía líquida de alta presión, la cromatografía bajo argentación, la calorimetría, la microscopía por difracción de rayos X y la espectrometría por resonancia magnética nuclear, han permitido entender los factores que gobiernan este proceso, lo cual ha sido fundamental para optimizarlo y para obtener productos con mayor valor agregado. Los esfuerzos de los fabricantes de equipos se centran en optimizar el sistema de enfriamiento y mejorar la selectividad del proceso, para obtener productos que se adapten a múltiples necesidades de la industria de alimentos y, muy particularmente, que reemplacen a y compitan ventajosamente con la manteca de cacao. En Colombia se fracciona casi el 80% del aceite de palma que se consume (unas 320.000 toneladas anuales), pero sectores industriales, como el de jabones, podrían absorber unas 30.000 toneladas de estearinas al año; para satisfacer estas demandas, así como la que originaría el desarrollo de la oleoquímica, sería necesario fraccionar otras 250.000 toneladas anuales de aceites de palma y palmiste.

Summary

Even though since the beginning of the XIX Century second half, fat fractionation was practiced in order to obtain "oleomargarine" and that in 1921 a semi-continuous process to separate oils from stearins using centrifuge splitters was already patented, oils and fats fractionation only started to gain industrial importance after 1950, and especially from 1970 on, thanks to the palm oil boom in countries such as Malaysia and Indonesia. Developments in other industrial sectors and the advent of analytical techniques like high pressure liquid chromatography, chromatography under argentation, X-rays defraction microscopy, and nuclear magnetic resonance spectrometry, have made it possible to understand this process governing factors, which has been basic to optimize it and to get greater added value products. The efforts realized by the equipment manufacturers are focused in the optimization of cooling systems and in

Palabras Clave

Aceite de palma,
Aceite de palmiste,
Fraccionamiento,
Usos.

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improving the process selectivity to obtain products that adapt to the multiple needs of the food industry, and in particular, that will replace and compete with cocoa butter. In Colombia, approximately 80% of the palm oil consumed (about 320,000 annual tons) is fractionated, but industrial sectors like the soap one, very well absorb about 30,000 stearin tons per year; in order to satisfy that demand, as well as the one that could be originated by the development of the oleochemistry, it would be necessary to split another 250,000 tons of palm oil and palmiste oil per year.

Introducción

Aun cuando los principales procesos utilizados actualmente para modificar las propiedades físicas de los aceites y grasas (hidrogenación, interesterificación, fraccionamiento) se conocen desde finales del siglo XIX o comienzos del siglo XX, su utilización a gran escala sólo vino a darse en años posteriores a 1950, como consecuencia del gran desarrollo que a partir de dicho año tuvo el cultivo de palma de aceite, especialmente en Malasia y posteriormente en Indonesia, Costa de Marfil, Costa Rica, Ecuador y Colombia, entre otros.

Según Colom Virgili (1), el fraccionamiento del sebo tiene su origen en la investigación llevada a cabo por Mège-Mouriès a partir de 1869 para ganar el premio ofrecido por el gobierno francés "para el que preparase una materia grasa que pudiera sustituir a la manteca de vaca, que resultase a un precio inferior que ésta y que se conservase bien"; este investigador trabajó con sebo fresco de bovinos, el cual dejaba enfriar en recipientes de gran superficie y poca profundidad; el cuajo que se formaba al cabo de 24 horas lo envolvía en lienzo, dejaba escurrir la parte líquida y luego lo prensaba siempre a una temperatura entre 20 y 25°C; con la presión salía a través del lienzo la llamada oleomargarina, de consistencia y aspecto como de una pomada y más parecida a la grasa de leche que la grasa original; dentro del lienzo quedaba la llamada oleoestearina, que por su consistencia no encontró uso inmediato en la preparación de alimentos y se utilizaba para fabricar bujías.

Este procedimiento se continuó utilizando hasta mediados del siglo XX, pero ya en 1921 Cyrus Howard Hapgood (The De Laval Separator Company) (2) patentó en Estados Unidos el primer proceso para la "separación de aceite y estearina de las grasas", utilizando separadoras centrífugas; en su solicitud de patente, Hapgood indica que la grasa debe enfriarse lentamente desde 60°C hasta 32°C en un tanque con agitación y establece la necesidad de controlar

en forma muy precisa esta última temperatura para que la separación sea eficiente.

Aun cuando el señor Hapgood no menciona qué tipo de grasas utilizó, ni qué rendimientos obtuvo, ni las características de las fracciones obtenidas, no hay duda de que contribuyó enormemente a los que hoy se consideran métodos modernos de fraccionamiento de grasas.

El fraccionamiento de aceites se ha visto favorecido por otros desarrollos industriales en empresas afines o diferentes al sector de aceites comestibles, entre los cuales vale la pena destacar el cristizador esbelto, patentado en los Estados Unidos por Frank R. Shuman y Chester Springs, de la Sun Oil Company (empresa petrolera) en 1959 para cristalizar las parafinas (3) y separarlas del petróleo; el filtro rotatorio bajo vacío, patentado en 1959 por Frank William Young (4); el filtro de cinta (florentino), patentado por Sark Pashaian y James Morrison Stewart (5) en 1967, y el filtro de membrana patentado por Kataoka Atsushi en 1991 (6).

Paralelamente a estos desarrollos, la producción de aceite de palma se hizo cada vez más importante y en 1972 la firma Tirtiaux, originalmente dedicada a la producción de margarinas en Fleurs (Bélgica), vendió su primera planta para fraccionar aceite de palma a una empresa en Costa de Marfil, aplicando una tecnología desarrollada por ellos desde 1950 y que había comercializado en Australia (1965) y Colombia (1967) para fraccionar sebo; en estas plantas se utilizaban cristalizadores verticales de gran capacidad en donde el aceite se enfriaba lentamente (8 horas) bajo agitación, así como filtro - prensas de tornillo para efectuar la separación de las fracciones.

Las investigaciones que se adelantan desde hace más de cincuenta años sobre las características de los aceites de palma y palmiste y el advenimiento de técnicas como la cromatografía líquida a alta presión (HPLC), la cromatografía bajo

argentación, la microscopía electrónica por difracción de rayos X, la calorimetría y la determinación del contenido de sólidos en grasas mediante resonancia magnética nuclear, han permitido esclarecer los factores que tienen mayor importancia en el proceso de cristalización, lo cual ha sido básico para desarrollar procesos más eficientes, menos costosos, así como productos con mayor valor agregado.

Fraccionamiento en seco de aceite de palma

El aceite de palma está compuesto fundamentalmente por ácido palmítico (42-46%) y ácido oleico (36-41%), así como por cantidades menores de los ácidos linoleico, linolénico y mirístico; a pesar de la gran cantidad de triacil glicerol que pueden formar estos ácidos, sólo seis de ellos juegan un importante papel en el fraccionamiento de este aceite (POP=23,7%; POS=5,7%; PPO=4,4% y POO=20,3%; PLP=6,5%; StOO=2,4%) (7); los tres primeros son los que le comunican al aceite de palma su naturaleza sólida mientras que los otros tres son los responsables de su

naturaleza líquida. En la Tabla 1 se muestra la composición del aceite de palma en términos de la insaturación de las moléculas, determinada por HPLC bajo argentación; los aceites duros tienen altos niveles de triacilglicerol de los tipos SSS, SOS y SSO, mientras que los aceites blandos son ricos en triacil glicerol de los tipos SLS y SOO. Debido a las diferencias entre los puntos de fusión de estos grupos, el aceite de palma puede ser fácilmente fraccionado en términos de ellos; sin embargo y dependiendo del tipo de fracciones que se quieran obtener, se deben buscar condiciones que permitan obtener una adecuada selectividad.

La mezcla de triacilglicerol presentes en el aceite de palma hace que éste no tenga realmente un punto de fusión definido, sino un rango que es bastante amplio, pues mientras el punto de fusión del triacilglicerol SSS es de 60°C, el del POP es 38°C y el del OOO es 4°C; lo anterior se hace evidente al estudiar el perfil de fusión determinado por Espectrometría NMR (Fig. 1) y es gracias a ello que este aceite es especialmente apto para ser sometido a fraccionamiento.

Esta misma mezcla es responsable de que el aceite de palma no cristalice a una determinada temperatura; a medida que se reduce la temperatura desde la máxima de fusión, empezarán a cristalizar los triacil glicerol trisaturados, luego los disaturados, luego los monosaturados y si se controla adecuadamente la temperatura, se podrá lograr que aquellos que lo hacen a temperaturas inferiores permanezcan líquidos, pudiéndose entonces separar por algún método físico (filtración, prensado, centrifugación).

Tabla Composición en triglicéridos del aceite de palma, según su grado de insaturación

Tipo de triglicérido	Estado físico a temp. ambiente	Aplicación	%*
SSS	Sólido	Producción de ácidos grasos	0.1
MPP			2.0
PPP		Coberturas duras	0.7
PPS			0.6
SSS			0.2
SUS	Semisólido	Chocolatería	28.7
POP			4.2
POS			0.2
SOS			11.0
PLP			23.7
SUU	Semilíquido	Margarinas	1.8
POO			10.9
SOO			3.6
PLO			3.3
PLL			1.8
UUU OOO	Líquido	Aceites para ensalada y para freír	0.5
OOL			6.7
OLL			
MG/DG			

* Aceite de palma de Malasia.

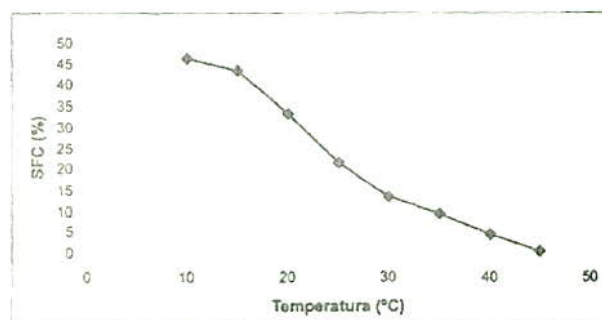


Figura 1 Perfil de fusión del aceite de palma



Los estudios calorimétricos (DSC) han permitido comprobar que aun cuando en el aceite de palma hay seis principales triacil gliceroles diferentes por su grado de insaturación, el termograma correspondiente sólo presenta dos grupos de picos diferenciables tanto durante el enfriamiento como durante el calentamiento, los cuales representan, claramente, los dos grupos de fracciones (líquidas y sólidas) que se pueden separar.

Otro elemento de análisis tiene que ver con las formas cristalinas de los triglicéridos; tradicionalmente se ha considerado que los triglicéridos adoptan tres formas cristalinas o polimorfos. Estos polimorfos, en orden creciente de estabilidad termodinámica y punto de fusión, se denominan como α , β' y β ; adicionalmente, en varios triglicéridos se ha encontrado una nueva forma denominada sub α o $\beta'2$; el aceite de palma presenta todas estas formas cristalinas, aun cuando tradicionalmente se ha dicho que lo hace en la forma β' , por cuanto es relativamente estable en dicha forma.

Un enfriamiento muy rápido del aceite líquido conduce a la forma sub α , la cual, por calentamiento, se transforma en la forma α ; un enfriamiento más lento conduce a la forma α , la cual, por calentamiento, se convierte en la forma β' ; enfriando a una temperatura por encima del punto de fusión de la forma α , se obtiene el polimorfo β' ; la forma β se obtiene por calentamiento de la forma β' , o por un enfriamiento lento.

Usando las condiciones adecuadas de enfriamiento, los polimorfos pasarán a través de transformaciones irreversibles, de las formas menos estables a las más estables, es decir, sub $\alpha < \alpha < \beta' < \beta$.

El comportamiento polimórfico, las características de cristalización y fusión específicas del aceite de palma se deben al comportamiento de fases determinado por los triacilgliceroles que lo componen y cada triacilglicerol actúa de manera diferente con los demás; algunos TAG en el estado líquido pueden actuar como solventes de TAG que estén en estado sólido, y algunos diagramas binarios de dos TAG presentan puntos eutécticos y peritéticos; POP muestra, con PPP, un comportamiento monotético con una solución parcial de sólido.

El alto contenido en los TAG PPP, POP y POO del aceite de palma conduce a la presencia de una mezcla eutéctica con dos fases de soluciones sólidas; la fase de alto punto de fusión está compuesta por POP y PPP, mientras que la fase de bajo punto de fusión contiene principalmente POO; tanto POP como PPP son estables en la forma β , pero debido a las interacciones entre TAG, la forma que predomina es la $\beta'1-2$.

Estudios recientes (8) muestran que la presencia de 1-2 y 1-3 digliceroles, los cuales se forman debido a la hidrólisis que sufre el aceite antes de ser refinado, pueden afectar la cristalización del aceite de palma, lo cual se ha comprobado indirectamente mediante la determinación del contenido de grasa sólida (SFC) en muestras a las cuales se les han añadido cantidades predefinidas de tales digliceroles.

El fraccionamiento en seco está compuesto por dos operaciones fundamentales: el enfriamiento y la separación de las fracciones.

El aceite de palma, usualmente RBD (aun cuando puede fraccionarse crudo) se calienta a una temperatura suficientemente alta (usualmente 70-80°C) con el fin de fundir toda la grasa sólida y remover los núcleos de cristales, lo cual garantiza que la cristalización es controlable y reproducible; existen dos técnicas ligeramente diferentes, de acuerdo a los equipos que se utilicen, la principal diferencia entre ellas radica en la velocidad de enfriamiento: mientras que Extraction De Smet, CMB, Oilteck y Krupp producen equipos que producen un enfriamiento rápido, Tirtiaux usa una cristalización lenta, lo cual parece ofrece una mejor separación de las fases (estearina y oleína).

Algunos desarrollos efectuados para mejorar la eficiencia del enfriamiento tienen que ver con la utilización de serpentines internos a través de los cuales circula el medio refrigerante (Oilteck), o con serpentines verticales que giran dentro del cristizador (Krupp).

El aceite se somete a sucesivas etapas de enfriamiento y retención, con agitación constante o no, hasta alcanzar la temperatura óptima para que los cristales formados crezcan y sean fáciles de separar de la fase que permanece líquida (5-8 horas).

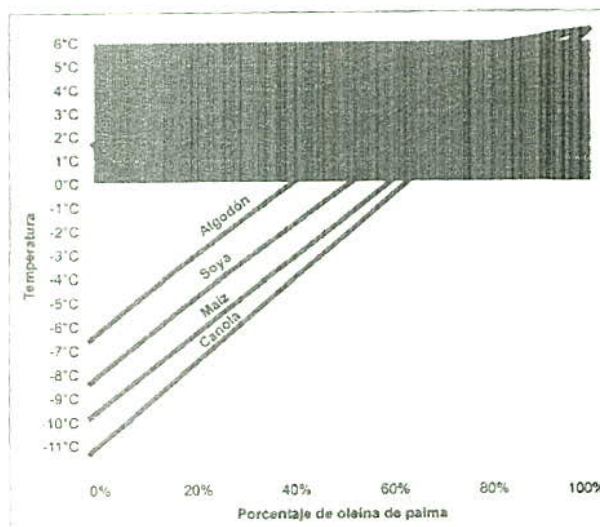
La separación de las fracciones se puede hacer por varios medios: filtro rotatorio bajo vacío, filtro de cinta continua (florentino), filtro prensa de placas o filtro de membrana.

Idealmente, debería ser posible separar totalmente las dos fracciones; sin embargo, la separación puede ser una etapa difícil de efectuar, pues la estructura de los cristales es tal que dentro de ellos puede quedar ocluida oleína y, adicionalmente, dependiendo de la forma y tamaño de los cristales también quedará oleína atrapada entre ellos; normalmente, el filtro rotatorio hace que quede mayor cantidad de oleína retenida por la torta de estearina, que el filtro florentino o el filtro de membrana; la dureza de la estearina dependerá entonces de la cantidad de oleína retenida. El rendimiento de oleína y la suavidad o dureza de la estearina dependerá del sistema de separación que se use, a iguales condiciones de enfriamiento.

En el caso del aceite de palma el interés se centra fundamentalmente en el rendimiento y calidad de la oleína obtenida, aun cuando en años recientes la obtención de grasas especiales para chocolatería y *shortenings* a partir de la estearina han hecho que también se preste atención a esta fracción.

Respecto a la oleína, se busca no sólo obtener rendimientos que lleguen hasta el 80%, sino puntos de nube (*cloud point*) lo más bajos posibles para poderla utilizar como aceite para freír o de ensalada; normalmente en una sola etapa de fraccionamiento es posible obtener oleínas con un punto de nube de hasta 4,5-5°C, las cuales, sin embargo, no cumplen satisfactoriamente el *Cold Test* (5,5 horas a 0°C), por lo cual se hace necesario mezclarla en diferentes proporciones con aceites más insaturados como los de soya, maíz, canola, etc., pudiéndose diseñar diferentes formulaciones, como se indica en la Figura 2.

Otra alternativa para mejorar el punto de nube y la estabilidad frente al frío de la oleína, consiste en someterla a nuevos fraccionamientos, pudiéndose obtener superoleínas con puntos de nube del orden de 2°C o las llamadas *top oleins*, las cuales se pueden utilizar sin mezclar para la preparación de ensaladas pues cumplen satisfactoriamente el *Cold Test*. En estos refraccionamientos de la oleína se obtiene una



Fuente: www.mpop.gov.my

Figura 2 Punto de nube de mezclas de oleína de palma con otros aceites

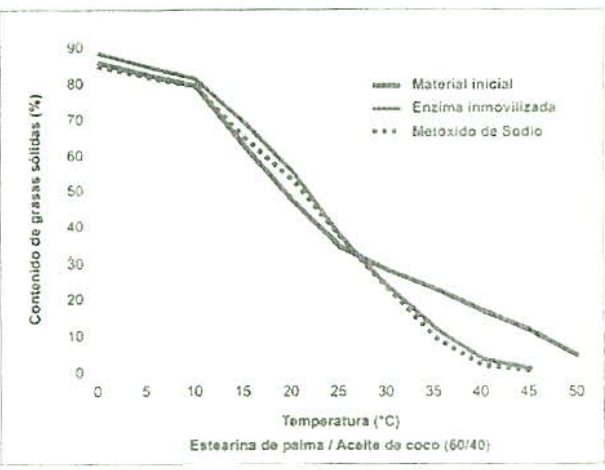
fracción intermedia conocida como *palm mild fraction* (PMF), la cual encuentra aplicación en la elaboración de *shortenings*, margarinas y equivalentes de la manteca de cacao (CBE).

Igualmente, se ha comprobado que si se parte de un aceite de palma neutralizado y desgomado y la oleína se somete a fraccionamiento múltiple, el betacaroteno se va concentrando progresivamente en la fracción de oleína, pudiéndose obtener una *top olein* con un contenido de betacarotenos superior a 800 ppm, lo cual la convierte en un producto de alto valor agregado (*golden olein*).

En algunas ocasiones, especialmente cuando se desea obtener grasas especiales para *shortenings*, margarinas o chocolatería, es importante recurrir a las fracciones intermedias o *palm mild fractions*, tanto a partir de la oleína como a partir de la estearina; para la producción de equivalentes de la manteca de cacao es particularmente deseable utilizar las PMF, las que, hasta hace unos años, debían obtenerse mediante fraccionamiento húmedo o con ayuda de solventes. En el caso de partirse de la estearina, un primer fraccionamiento permitirá separar una estearina dura rica en PPP, así como una oleína que, sometida a un nuevo fraccionamiento, producirá una segunda estearina rica en POP.

Tabla 2 Interesterificación de estearinas de palma con grasas exóticas

	Monosaturados				Monoinsaturados						Diinsaturados						Poliinsaturados			
	PPP	PPS	PSP	TOT	POM	POP	POS	SOS	SOA	TOT	POO	SOO	PLIP	PLIS	SLIS	TOT	OOO	PLIO	SLIO	TOT
Manteca de cacao	Tr	Tr		Tr	0.5	16	36	30	2	84.5	2	3.5	2.5	4	1.5	13.5	0.4	0.9	0.3	1.6
PMF	1.5	Tr	-	1.5	2.3	42	8	0.7	-	53	18.4	1.9	11.3	Tr	Tr	31.6	2.9	9.3	-	12.2
Mango Fat				0.9		9.5	51.7	3.7	65.8	1.2	22.7		0.9		24.8	3.4	2.9	0.4	6.7	
Illipe Fat					7.1	31.4	49.9	2.4	90.8	1.5	3.1	0.4	1.2	0.8	7	7	0.8	0.6	8.4	
Shea stearine					1.4	9.9	65.5	3.9	80.7	0.6	7.4		1.6	8	17.6	0.8		1.2	2	



Fuente: www.novozymes.com

Figura 3 Perfil de fusión de estearina de palma interesterificada con aceite de coco

Estas estearinas, con un índice de yodo entre 34 y 36 presentan a temperaturas bajas un contenido de sólidos muy similar al de la manteca de cacao, pero a temperaturas de 37-38°C presentan un contenido mayor, lo cual es un demérito cuando se trata de utilizarlas para reemplazar la manteca de cacao; para obviar esta diferencia, se puede recurrir a la interesterificación con aceites líquidos o con aceite de coco o de palmiste, con lo cual y como se muestra en la Figura 3, se mejora sustancialmente este aspecto. Sin embargo, la mezcla o interesterificación con grasas láuricas puede disminuir la compatibilidad con la manteca de cacao.

Para obviar lo anterior, se han obtenido buenos resultados mezclando o interesterificando estas estearinas con algunas grasas exóticas como las obtenidas de *shea*, *illipe*, *salt* o mango, las cuales, por su alto contenido de POP, mejoran notable-

mente el desempeño, pues permiten mezclarlas con manteca de cacao en todas las proporciones (Tabla 2) (9).

La estearina dura de palma (IV < 20) se puede utilizar para reemplazar aceites hidrogenados en shortenings y margarinas como las que se requieren para la elaboración de pastas de hojaldre (*puff pastry*) y encuentra también aplicaciones en usos industriales como la obtención de jabones, ácido esteárico, estearatos de glicerilo así como metilésteres alfa sulfonados, los cuales pueden reemplazar eficientemente a los derivados del ácido bencen-sulfónico lineal en la fabricación de detergentes en polvo, jabones en barra y cremas lava loza.

Fraccionamiento en seco de aceite de palmiste

A diferencia del aceite de palma, que contiene cantidades casi iguales de ácidos grasos saturados e insaturados, el aceite de palmiste está conformado fundamentalmente por ácidos grasos saturados (mirístico, láurico, palmítico y esteárico), los cuales representan hasta el 75-83% de todos los ácidos grasos en él presentes; como ácidos grasos insaturados están presentes el ácido oleico (14-16%) y el ácido linoleico (2-4%) (10).

El análisis por HPLC muestra también una alta concentración de triacilgliceroles trisaturados y diinsaturados, y el análisis calorimétrico muestra que si bien se forman dos grupos de picos tanto durante el enfriamiento como durante el calentamiento, éstos aparecen casi superpuestos; por último, el perfil de sólidos (SFC) muestra que el paso de la fase sólida a la fase líquida ocurre en un rango de temperatura muy pequeño (Fig. 4).

Lo anterior constituye una gran dificultad para someterlo a fraccionamiento en seco, por lo que

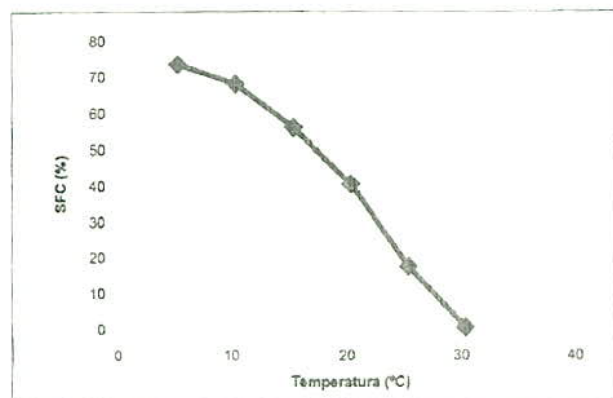


Figura 4 Perfil de fusión del aceite de palmiste

generalmente se acostumbra enfriarlo en bandejas de poca profundidad hasta temperaturas de 22–25°C, envolver la masa cristalizada en lonas y someterlo a prensado en prensa tipo vertical; este proceso es bastante intensivo en mano de obra pero no requiere de equipos muy sofisticados y puede producir aproximadamente un 45% de estearina, dependiendo de la temperatura de enfriamiento y de la presión aplicada.

Alternativamente, se pueden utilizar solventes (acetona) o detergentes (lauril sulfato de sodio) para disminuir la relación sólido-líquido de la masa cristalizada, disminuir la tensión interfasial y facilitar la filtración; en ambos métodos se acostumbra también recircular parte de la oleína para disminuir la relación sólido-líquido; estos dos sistemas son costosos, exigen equipos más sofisticados con medios para separar el solvente o el detergente de las fracciones separadas, pero permiten obtener una mejor separación de las fases y mayor selectividad.

En el fraccionamiento del aceite de palmiste la fracción de interés es la estearina, por presentar un perfil de fusión muy similar al de la manteca de cacao, lo cual la hace especialmente atractiva para reemplazarla en productos de chocolatería, confitería, rellenos dulces y coberturas de helado; sin embargo, este producto no es compatible con la manteca de cacao y debe utilizarse sólo como sustituto total.

Tanto el aceite entero como sus fracciones se utilizan para disminuir el contenido de sólidos a

temperaturas entre 35 y 38°C de *shortenings* y margarinas para untar, mediante interesterificación con estearinas duras obtenidas por fraccionamiento de aceite de palma. La gran ventaja de estos productos frente a los elaborados a partir de aceites parcialmente hidrogenados es su casi nulo contenido de isómeros *trans*, los cuales han sido cuestionados por su posible incidencia sobre las enfermedades coronarias.

En Europa se acostumbra además hidrogenar tanto la estearina como la oleína de palmiste hasta índices de yodo inferiores a uno, existiendo una gran variedad de productos de este tipo diseñados para diferentes aplicaciones y climas.

Con todo, vale la pena comentar que el aceite de palmiste encuentra su mayor aplicación en la elaboración de jabones por su capacidad detergente y espumante, así como en la elaboración de una gran cantidad de derivados oleoquímicos como el alcohol laurílico y diversos lauril-sulfatos de gran importancia en la elaboración de productos de limpieza y cuidado personal.

Desarrollos recientes

Como se comentó anteriormente, el fraccionamiento del aceite de palmiste presenta serias dificultades por el estrecho margen de temperatura dentro del cual se mantiene líquido; de igual manera, se presentan dificultades en el refraccionamiento de las estearinas de palma, por la alta viscosidad de la masa cristalizada, lo cual dificulta su transporte hasta la estación de filtrado.

Dos empresas, una japonesa -Fuji Oil Company- (11) dedicada a la producción de aceites, y otra belga -De Smet Engineering N.V.- (12), fabricante de equipos, han patentado por separado un método para obviar este problema, el cual consiste en cristalizar muy lentamente la masa de aceite previamente fundida dentro de recipientes de poco espesor (horizontal o vertical), usando como medio refrigerante aire o agua y sometiendo luego la masa cristalizada a una fuerza de corte mecánico (tritución, batido), con lo cual la masa cristalizada se vuelve fluida, pudiéndose bombear hacia un filtro prensa (mecánico o tipo membrana) en donde se realiza la separación de las fracciones.

Mientras los investigadores japoneses restringen el uso de la técnica a aceites con bajo contenido de ácido láurico y utilizan aire como medio refrigerante, los belgas no los excluyen, y por el contrario, manifiestan haber obtenido estearinas de palmiste con un índice de yodo bastante bajo y utilizan agua como medio refrigerante.

Las principales etapas del proceso patentado por De Smet se resumen así:

1. Fusión del aceite a temperaturas suficientemente altas para garantizar la destrucción de todos los cristales
2. Precristalización del aceite en cristalizadores convencionales (hasta alcanzar, por ejemplo, un 1% de sólidos)
3. Cristalización lenta de la masa dentro de un conjunto de bandejas verticales de no más de 10 cm de espesor, por entre cuyas paredes fluye un medio refrigerante, mantenidas herméticas mediante un sistema de presión similar al de un filtro-prensa (Figura 5), durante 4-6 horas

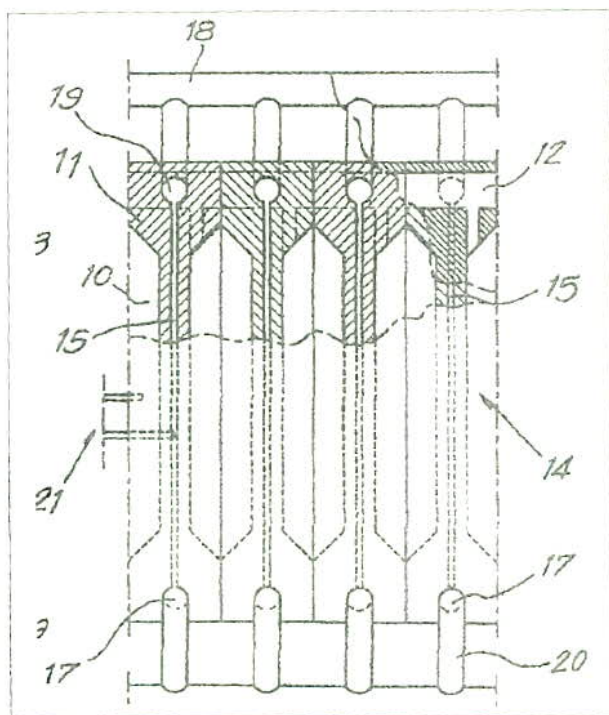


Figura 5
Cristalizador de placas De Smet (Patente EP 1 281 749 A1)

4. Apertura de las cámaras y descarga de los bloques cristalizados dentro de una tolva que los conduce a un triturador
5. Trituración de los bloques, con lo cual el producto adquiere fluidez, pudiéndose enviar usando una bomba de tornillo al separador
6. Separación de las fracciones usando filtro de membrana a una presión de 25-28 bars.

Algunos de los resultados obtenidos se muestran en la Tabla 3.

Tabla 3
Fraccionamiento de aceite de palmiste de acuerdo a la patente EP 1 281 749 A1

Periodo de cristalización (horas)	2,0	3,5	5,0
Temperatura del agua de enfriamiento (°)	18	20	22
SFC del material cristalizado	24	23	23
Rendimiento de estearina	38	35	31
SFC calculado para la estearina	63	66	64
Índice de yodo de la estearina	8,9	5,2	4,4

Aun cuando esta tecnología es aparentemente un regreso a los comienzos del proceso y requiere grandes instalaciones por la baja capacidad de cada una de las celdas de enfriamiento, hace un aporte significativo al fraccionamiento del aceite de palmiste y al refraccionamiento de estearinas, permitiendo la fluidización de la masa cristalizada y la liberación de las oleínas sin destruir los cristales, facilitando así la separación de las fracciones.

Potencial del fraccionamiento de aceites de palma y de palmiste en Colombia

En Colombia se consumen anualmente unas 450.000 toneladas de aceite de palma (13) de las cuales se fracciona aproximadamente el 80% (360.000 toneladas), así como 21.000 toneladas de palmiste, del cual no se tiene información sobre su fraccionamiento.

El objetivo principal del proceso en el país es la producción de oleínas con puntos de nube entre 4,5 y 5,5°C, las cuales se mezclan en diferentes proporciones con aceite de soya para producir aceites de mesa y cocina, o se comercializan sin mezclar para freído en zonas cálidas.

Las estearinas, cuyo índice de yodo oscila entre 44-48 se utilizan fundamentalmente para

producir mantecas vegetales y margarinas, mezclándolas con aceite de palma entero o con aceite de palmiste, sin interesterificar; una pequeña cantidad se dedica a la producción de jabones y ácido esteárico.

Hasta donde se sabe, ninguna empresa realiza refraccionamientos de oleína y estearina en gran escala y posiblemente sólo una ha hecho ensayos de interesterificación para producir equivalentes de la manteca de cacao.

En cuanto al aceite de palmiste, una pequeña cantidad se utiliza en la elaboración de mantecas vegetales, margarinas de mesa y cocina, así como margarinas de panificación; el resto se utiliza principalmente para aplicaciones industriales (jabonería).

Un estudio reciente (14) muestra que en el país existe una demanda potencial de unas 30.000 toneladas anuales de estearina por parte de las empresas del sector de productos de aseo, así como unas 5.000 toneladas de mezclas de estearina de palma con aceites de palma y palmiste. Para satisfacer esta demanda sería necesario fraccionar unas 130.000 toneladas anuales adicionales de aceite de palma, generándose, igualmente, 100.000 toneladas anuales de oleína.

Existe, por lo tanto, un potencial interesante por desarrollar, para lo cual sería conveniente realizar estudios tanto a nivel país como a nivel de las diferentes regiones palmeras, con el fin de determinar las alternativas más favorables para atender esta demanda, lo cual conduciría a un importante incremento del consumo interno.

Es importante tener en cuenta que se pueden explorar muchas alternativas, tales como la producción de superoleínas u oleínas *top*, así como oleínas ricas en vitamina E y beta caroteno, y fracciones intermedias y sustitutos o equivalentes de mantecas de cacao con destino al mercado externo, existiendo muchos modelos para analizar, partiendo de la ecuación básica de costos de producción, en la cual se asigna un costo a una de las fracciones y se calcula el de la otra mediante la expresión

$$SC = \frac{SA + (\$mo + \$if) - X * (SB)}{100 - X/100}$$

en donde

\$A = costo del aceite a fraccionar (\$/kg)

\$mo = costo mano de obra del proceso (\$/kg)

\$if = costos indirectos de fabricación del proceso

X = rendimiento de la fracción B (%)

\$B = costo asignado a la fracción B

\$C = costo de la fracción C

Dependiendo entonces de cómo se valore una de las fracciones se calculará el costo de la otra, como se ilustra en la Figura 6, suponiendo que los costos y rendimientos de proceso se mantienen constantes; si, por ejemplo la fracción B es una PMF que pueda comercializarse a un precio elevado, se le podrá asignar un costo mayor y entonces, la superoleína correspondiente podrá costar menos que la oleína de la cual proviene.

El establecimiento de nuevas instalaciones de fraccionamiento de los aceites de palma y palmiste en el país, o la optimización de las actualmente instaladas, es una opción que vale la pena analizarse y evaluarse, pues hasta ahora los industriales se han concentrado básicamente en el fraccionamiento primario y existen muchas alternativas para desarrollar productos con mayor valor agregado, tanto para el mercado doméstico como de exportación, que contribuirían a una mayor absorción de la producción nacional de estos aceites.

Para que tales desarrollos se materialicen, es necesario que se fortalezcan las relaciones entre

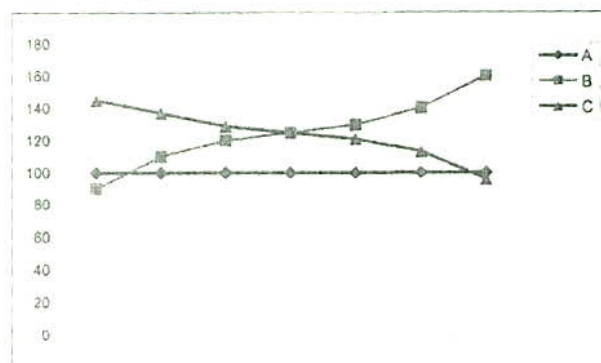


Figura 6 Costo relativo de fracciones

los eslabones de esta cadena agroindustrial para acometer, conjuntamente, proyectos de riesgo y beneficios compartidos.

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LA MEJOR OPCIÓN EN LOGÍSTICA Y TRANSPORTE

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PRODUCTOS Y SERVICIOS

Aceites y Derivados

ACEITE CRUDO DE PALMA

Descripción
Se obtiene del mesocarpio de la fruta de la palma de aceite, *Elaeis guineensis* Jacq. y sus variedades, por proceso de extracción mecánica o por solventes. Se caracteriza por tener una relación 1,1 de ácido palmítico y ácido oleico, lo cual le imprime una alta estabilidad a la oxidación y no requiere de hidrogenación (proceso precursor de ácidos grasos trans). Además, tiene un alto contenido de vitaminas A (carotenos) y vitaminas E (Tocóferoles y Tocotrienoles).



Uso sugerido
El aceite crudo de palma se utiliza en su forma natural como materia prima en la industria de aceites y grasas comestibles (aceites líquidos y margarinas), concentrados para animales, jabones, biodiesel, entre otros.

Gracias a su relación de ácidos grasos, del aceite se obtiene dos fracciones: estearina y oleína, las cuales tienen un amplio rango de usos a nivel industrial.

[Arriba »](#)

ACEITE DE PALMA ALTO OLÉICO

Descripción
Aceite extraído del fruto de la palma de aceite variedad híbrido *Elaeis guineensis* Jacq x *Elaeis Oleifera*, por procesos de extracción mecánica o por solventes. Se caracteriza por tener un alto contenido de oleína (alrededor del 85%), vitamina A (Carotenos) y vitamina E (Tocóferoles y Tocotrienoles).

Uso sugerido
Es reconocido como el sustituto tropical del aceite de oliva, tiene un mejor perfil nutricional que el de la palma africana, comenzando por un contenido de ácidos saturados 6% inferior. Su alto contenido de ácidos grasos mono y poli insaturados ayudan a disminuir los niveles de lipoproteínas de baja densidad (colesterol malo) y equilibran los niveles de lipoproteínas de alta densidad (colesterol bueno).



[Arriba »](#)



- ACEITES Y DERIVADOS
- INSUMOS AGROINDUSTRIALES
- SERVICIOS



Hoja Técnica de Seguridad del Material

Código del producto: 201012

Fecha de revision: 09-may-2006

1. IDENTIFICACION DE LA SUBSTANCIA/PREPARADO Y DE LA SOCIEDAD/EMPRESA

Código del producto: 201012

Nombre del producto: TRIPALMITIN

Sinónimos: Heaxadecanoic acid 1,2,3-propanetriyl ester; Palmitin; Glyceryl tripalmitate

Proveedor:

MP Biomedicals, LLC

29525 Fountain Parkway

Solon, OH 44139

tel: 440-337-1200

Teléfono de emergencia: CHEMTREC: 1-800-424-9300 (1-703-527-3887)

2. COMPOSICION/INFORMACION SOBRE LOS COMPONENTES

Componentes	CAS Number	% en peso	ACGIH Exposure Limits:	Osha pel 8 hr. twa (mg/m³):
TRIPALMITIN	555-44-2	90 - 100%	Ninguno(a)	Ninguno(a)

3. IDENTIFICACION DE LOS PELIGROS

Perspectiva General de Emergencia: Puede causar irritaciones en la piel y/o dermatitis

Principales vías de exposicion: Piel

Inhalación: Puede producir irritaciones en el sistema respiratorio

Ingestión: Puede ser nocivo si es tragado.

Contacto con la piel: Puede provocar una reacción alérgica de la piel

Contacto con los ojos: Evítese el contacto con los ojos

Declaraciones de peligro Puede provocar una reacción alérgica de la piel.

Statement of Spill or Leak - ANSI Label Eliminate all ignition sources. Absorb and/or contain spill with inert materials (e.g., sand, vermiculite). Then place in appropriate container. For large spills, use water spray to disperse vapors, flush spill area. Prevent runoff from entering waterways or sewers.

4. PRIMEROS AUXILIOS

Consejo general: En caso de accidente o malestar, acuda inmediatamente al médico (si es posible, muéstrela la etiqueta).

Inhalación: Move to fresh air. Call a physician immediately.

Contacto con la piel: Enjuagar inmediatamente con abundancia de agua y recabar el consejo médico

Ingestión: No provocar vómitos sin consejo médico.

Contacto con los ojos: En caso de contacto con los ojos, lávenlos inmediata y abundantemente con agua y acúdase a un médico.

Protección de los socorristas: No hay información disponible

Condiciones medicas agravadas por la exposicion: No conocidos

Código del producto: 201012

Nombre del producto: TRIPALMITIN

Page 1 of 5

5. MEDIDAS DE LUCHA CONTRA INCENDIOS

Medio extintor apropiado:	Utilizar polvo químico seco, CO2, agua pulverizada o espuma de "alcohol"
Peligros específicos:	La combustión produce humos irritantes.
Peligros inusuales:	No conocidos
Equipo de protección especial para los bomberos:	Como en cualquier incendio, llevar un aparato respiratorio autónomo con demanda de presión, MSHA/NIOSH (aprobado o equivalente) y una ropa de protección total
Metodos específicos:	Los recipientes cerrados pueden enfriarse con agua nebulizada.
Punto de inflamación:	indeterminado
Temperatura de autoignición:	indeterminado
Indice NFPA:	
NFPA Health:	1
NFPA Flammability:	1
NFPA Reactivity:	0

6. MEDIDAS QUE DEBEN TOMARSE EN CASO DE VERTIDO ACCIDENTAL

Precauciones personales:	Utilícese equipo de protección personal.
Precauciones para la protección del medio ambiente:	Evite que el producto vaya al alcantarillado.
Métodos de limpieza:	Barrer y palear dentro de recipientes apropiados para su eliminación.

7. MANIPULACION Y ALMACENAMIENTO

Almacenamiento:	
ROOM TEMPERATURE	
Manipulación:	Utilizar solamente en áreas provistas de ventilación y extracción apropiadas.
Advertencia para la manipulación segura:	Llevar equipo de protección personal.
Productos incompatibles:	Productos oxidantes y espontáneamente inflamables

8. CONTROLES DE EXPOSICION Y PROTECCION PERSONAL

Disposiciones de ingeniería: Asegúrese una ventilación apropiada.

Protección personal

Protección respiratoria: Aparato de respiración si se forma aerosol.

Protección de las manos: Guantes de PVC u otro material plástico

Protección de la piel y del cuerpo: El seguimiento de las precauciones normales de seguridad durante la manipulación del producto le protegerán de este efecto potencial.

Protección de los ojos: gafas protectoras con cubiertas laterales

Medidas de higiene: Manipular con las precauciones de higiene industrial adecuadas, y respetar las prácticas de seguridad.



9. PROPIEDADES FISICAS Y QUIMICAS

Estado fisico:	sólido
Formula:	C51H98O6
Temperatura de fusión/rango:	66-67°C
Código del producto: 201012	Nombre del producto: TRIPALMITIN

Temperatura de ebullición/rango:	No Data available at this time.
Densidad:	sin datos disponibles
Presión de vapor:	sin datos disponibles
Indice de evaporación:	sin datos disponibles
Densidad de vapor:	sin datos disponibles
Solubility (in water):	insoluble
Punto de inflamación:	indeterminado
Temperatura de autoignición:	indeterminado

10. ESTABILIDAD Y REACTIVIDAD

Estabilidad:	Estable bajo las condiciones de almacenamiento recomendadas.
polimerización:	Nada en condiciones normales de proceso.
Productos de descomposición peligrosos:	La descomposición térmica puede llegar a desprender gases y vapores irritativos.
Materias que deben evitarse:	agentes oxidantes fuertes
Condiciones que deben evitarse:	Exposición al aire o a la humedad durante periodos prolongados.

11. INFORMACION TOXICOLOGICA

Información del Producto

Toxicidad aguda

Componentes
TRIPALMITIN

RTECS Number:
RT4953500

Selected LD50s and LC50s
indeterminado

Toxicidad crónica:	La exposición crónica puede causar náuseas y vómitos, la exposición más importante ocasiona inconsciencia.
Efectos locales:	Los síntomas por sobreexposición pueden ser dolor de cabeza, vértigo, cansancio, náuseas y vómitos.
Efectos específicos:	May include moderate to severe erythema (redness) and moderate edema (raised skin), nausea, vomiting, headache.
Irritación primaria:	No hay datos disponibles sobre este producto.
efectos carcinógenos:	No hay datos disponibles sobre este producto.
efectos mutágenos:	No hay datos disponibles sobre este producto.
Toxicidad a la reproducción:	No hay datos disponibles sobre este producto.

12. INFORMACIONES ECOLOGICAS

Movilidad:	sin datos disponibles
Bioacumulación:	sin datos disponibles
Efectos ecotoxicológicos:	sin datos disponibles
Toxicidad acuática:	Puede causar efectos adversos a largo plazo en el medio ambiente acuático.

Componentes	U.S. DOT - Appendix B - Marine Pollutan	U.S. DOT - Appendix B - Severe Marine Pollutants	United Kingdom - The Red List:
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista	No Puesto en Lista
Componentes	:	World Health Organization (WHO) - Drinking Water	Ecotoxicity - Fish Species Data
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista	No Puesto en Lista

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Componentes	Ecotoxicity - Freshwater Algae Data	Ecotoxicity - Microtox Data	Ecotoxicity - Water Flea Data
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista	No Puesto en Lista
Componentes	EPA - ATSDR Priority List	EPA - HPV Challenge Program Chemical List	California - Priority Toxic Pollutants
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista	No Puesto en Lista
Componentes	California - Priority Toxic Pollutants	California - Priority Toxic Pollutants	
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista	

13. CONSIDERACIONES SOBRE LA ELIMINACION

Desechos de residuos / producto no utilizado:	Waste disposal must be in accordance with appropriate Federal, State, and local regulations. This product, if unaltered by use, may be disposed of by treatment at a permitted facility or as advised by your local hazardous waste regulatory authority. Residue from fires extinguished with this material may be hazardous.
Envases contaminados:	No reutilizar los recipientes vacíos

14. INFORMACION RELATIVA AL TRANSPORTE

No. UN/ID:	no regulado
Dot:	
Denominación adecuada de envío:	no regulado

Componentes	U.S. DOT - Appendix A Table 1 - Reportable Quantities
TRIPALMITIN	No Puesto en Lista

Tdg (canada):	
Whmis clasificacion de peligro:	Non-controlled

IMO:	
IMDG - Hazard Classifications	No aplicable

Componentes	U.S. DOT - Appendix B - Marine Pollutan	U.S. DOT - Appendix B - Severe Marine Pollutants
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista

Etiquetas IMO:

15. INFORMACION REGLAMENTARIA

Inventarios Internacionales

Componentes
TRIPALMITIN

Código del producto: 201012

Nombre del producto: TRIPALMITIN

Page 4 of 5

Inventory - United States TSCA - Sect. 8(b)	Present
Inventario canadiense:	No Puesto en Lista
Lista canadiense de sustancias no dom�sticas:	C51H98O6
Inventarios qu�micos australianos:	Present
China:	Present
Einecs:	209-098-1; C51H98O6
:	KE-18032

Componentes	California Proposition 65	Ma ley de derecho a saber:	Lista derecho de informacion de nueva jersey:	Lista de derecho a la informacion de pensilvania:
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista	No Puesto en Lista	No Puesto en Lista
Componentes	:	:	Illinois - Toxic Air Contaminants	Connecticut - Hazardous Air Pollutants
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista	No Puesto en Lista	No Puesto en Lista
Componentes	:	:	NTP:	:
TRIPALMITIN	No Puesto en Lista	No Puesto en Lista	Ninguno(a)	Ninguno(a)

SARA 313 Notification: The above is your notification as to the SARA 313 listing for this product(s) pursuant to Section 313 of Title III of the Superfund Ammendments and Reauthorization Act of 1986 and 40 CFR Part 372.

If you are unsure if you are subject to the reporting requirements of Section 313, or need more information, please call the EPA Emergency Planning and Community Right-To-Know Information Hotline: (800) 535-0202 or (202) 479-2499 (in Washington, DC or Alaska).

State Notification: The above information is your notice as to the Right-to-Know listings of the stated product(s). Individual states will list chemicals for a variety of reasons including, but not limited to, the compounds toxicity; carcinogenic, tumorigenic and/or reproductive hazards; and the compounds environmental impact if accidentally released.

16. OTRAS INFORMACIONES

Preparado Por: Health & Safety

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Fin de la Ficha de Datos de Seguridad

Enzymatic Interesterification of Tripalmitin with Vegetable Oil
Blends for Formulation of Caprine Milk Infant Formula Analogs

C O Maduko C C Akoh Y W Park

Received 31 March 2006; accepted 16 August 2006

Abstract Full Text PDF Images References

Abstract

The structure of triacylglycerols in vegetable oil blends was enzymatically modified, and the blends were incorporated into skim caprine milk to produce goat milk-based infant formula analogs, homologous to human milk. A modified lipid containing palmitic, oleic, and linoleic acids, resembling the composition of human milk fat, was synthesized by enzymatic interesterification reactions between tripalmitin and a vegetable oil blend containing a 2.5:1:1.0:8 ratio of coconut, safflower, and soybean oils. A commercial *sn*-1,3-specific lipase obtained from *Rhizomucor miehei*, Lipozyme RM IM, was used as the biocatalyst. The effects of substrate molar ratio and reaction time on the incorporation of palmitic, oleic, and linoleic acids at the *sn*-2 position of the triacylglycerols were investigated. The fatty acid composition and *sn*-2 position of the experimental formulas were analyzed using gas chromatography. Results showed that the highest incorporation of palmitic acid was obtained at 12 h of incubation at 55°C with a substrate molar ratio of 1.0:4 of tripalmitin to vegetable oil blend. However, the modified milk interesterified for 12 h at a 1:1 molar ratio had a greater resemblance to human milk compared with the other formulas. The level of oleic acid incorporation at the *sn*-2 position increased with the molar ratio of tripalmitin to vegetable oil blend. It was concluded that, unlike the original goat milk and other formulas, the formulated caprine milk with a molar ratio of 1:1 and a 12-h incubation was similar to the fatty acid composition of human milk.

Key words: enzymatic interesterification, tripalmitin, vegetable oil blend, caprine milk

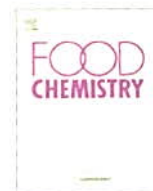
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Tripalmitin and monoacylglycerols as modifiers in the crystallisation of palm oil

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ABSTRACT

An exhaustive analysis of the crystallisation behaviour of palm oil was performed using low-resolution magnetic pulsed nuclear resonance, differential scanning calorimetry, polarised light microscopy and X-ray diffraction. The aim of this study was to characterise the changes induced in the crystallisation of palm oil by the addition of two different levels of tripalmitin and two different types of monoacylglycerols. The addition of monoacylglycerols led to the formation of a large number of crystallisation nuclei without changing the final solids content, accelerating the process of crystal formation, leading to the formation of smaller crystals than those found in the refined palm oil. Higher levels of tripalmitin produced crystals with larger dimensions, reducing the induction period and resulted in a higher level of solids at the end of the crystallisation period. The addition of monoacylglycerols and tripalmitin induced the formation of a polymorphic β -form.

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1. Introduction

The fatty acid composition of palm oil is characteristic and unique, containing approximately the same amounts of saturated and unsaturated fatty acids, particularly palmitic and oleic acids. Another relevant factor is the significant amount of saturated fatty acids (10–16%) located in the *sn*-2 position of the triacylglycerols, these being determinant with respect to the crystallisation properties. The triacylglycerols present are composed of 4.0–10.5% of tri-saturated, 41–59% of di-saturated–mono-unsaturated, 32–54% of mono-saturated–di-unsaturated and 3.0–12% of tri-unsaturated (O'Brien, 2004).

The types of nucleation involved in fat crystallisation are divided into primary and secondary nucleation, the first being subdivided into homogeneous and heterogeneous. Primary nucleation occurs not only at the beginning of the crystallisation process, but also parallel to secondary nucleation, being controlled by a sufficient amount of thermodynamic forces, such as subcooling or supersaturation. Most natural fats have sufficient amounts of minority lipids to influence this process. The secondary nucleation process is linked to crystal growth from the surface of previously formed structures, or parts of these, which may give rise to a crys-

talline network. A fat crystal network is formed by their aggregation, due to the attraction exerted by Van der Waal's forces. This union continues to grow until a three-dimensional network is formed. The crystals start to join up in the presence of small already-formed structures, until they become crystal structures of great volume, while the processes of nucleation and growth continue. A consequence of the simultaneous processes of crystallisation and aggregation is that even with low proportions of crystallised fat, a continuous network is formed. This process leads to the formation of solid bridges between crystals (sintering) and aggregated particles. The number, size and shape of the particles and the dimensions of the clusters will define the microstructure, which will determine the mechanical properties of the fat (Bois-telle, 1988; De Graef, Dewettink, Verbeken, & Foubert, 2006; Foubert, Dewettinck, Van de Walk, Dijkstra, & Quinn, 2007).

In a crystallisation process, the induction time may be defined as the time required to detect the formation of the first nucleus in a subcooled or supersaturated system. This period includes the actual time required for the nucleation, plus the time required to detect crystallisation using an experimental technique. Since subcooling is the temperature to which the triacylglycerol is cooled below the equilibrium temperature and leads to an increased nucleation rate and shorter nucleation time (Metin & Hartel, 2005), one may consider that the induction time usually increases with an increase in crystallisation temperature and decrease in sample melting point.

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Monoacylglycerols assume an important role in the crystallisation process. In some cases, when they are present at high levels or low temperatures, they generally contribute to the crystallisation process by increasing both the number of crystals and the nucleation rate. On the other hand, when they are present at low levels or higher temperatures, they will slow the crystallisation process down in a lipid material (Foubert, Vanhoutee, & Dewettinck, 2004).

Triacylglycerols levels in binary mixtures affect their crystallisation behaviour. Both the thermal behaviour observed by DSC and the polymorphism value by X-ray diffraction have changed for different fractions of tripalmitin blended with 1,3-dipalmitoyl-2-oleoyl-glycerol (POP) and 1,2-dioleoyl-3-palmitoyl-glycerol (POO) (Mihara, Ishiguro, Fukano, Taniuchi, & Ogino, 2007).

The lipid composition and crystallisation conditions influence the crystal format, and different polymorphic forms and crystal morphologies are possible. The crystals are aggregated into larger structures forming a network, which characterises the fat microstructural level. The type of polymorph characteristic of a fat or oil is dependent on the distribution of fatty acids in the triacylglycerol molecule, and the degree of randomisation is particularly important. In turn the microstructure concept includes information about the state, quantity, shape, size, spatial relationship and interaction amongst all the components of the crystalline network, and has an enormous influence on the macroscopic properties of the fats (Marangoni & Hartel, 1998; Ribeiro et al., 2009; Shi, Liang, & Hartel, 2005).

Although there are explanations about the mechanisms that determine the crystal type formed, there is little information about the way the presence of some compounds modifies crystal polymorphism. Knowledge of this effect could make it possible to control palm oil crystallisation, leading to its application in a huge variety of products and processes. The objective of this study was to make a complete characterisation of the changes caused in the crystallisation behaviour of refined palm oil by the addition of monoacylglycerols with different fatty acid compositions and two different levels of tripalmitin. The characterisation was made considering the thermogram and isothermal crystallisation, the kinetics and morphology of crystal formation and the polymorphic changes that occurred.

2. Materials and methods

2.1. Materials

Refined, bleached and deodorised palm oil (Po) were provided by national industry. Tripalmitin (PPP), 99% purity, was provided by Sigma-Aldrich (St. Louis, MO). Monoacylglycerols of fully hydrogenated palm oil (MP), 90% of theoretical purity and monoacylglycerols of behenic acid (MBe), 90% of theoretical purity, were used as commercial samples.

2.2. Sample preparation

2.2.1. Addition of acylglycerols

Four palm oil samples were prepared by adding tripalmitin (two different levels) and monoacylglycerols (behenic acid and full hydrogenated palm oil) to a Po sample.

Two different levels of PPP were added (5.7% and 11.4% of Po sample mass), resulting in final tripalmitin contents of 13.6% (PoTp1) and 17.8% (PoTp2). The palm oil samples were previously melted, tripalmitin was weighed on an analytical balance and added to the tubes with palm oil. The systems were shaken in shaker tubes for 30 s, heated at 100 °C for 30 min and shaken again for 30 s at around 100 °C, to ensure complete homogenisation.

Following the above procedure, 1.01% (m/m) of MP or MBe was added, resulting in PoMp and PoMBe samples, respectively, each one with 1.0% of monoacylglycerols regarding the final mass.

2.3. Analytical methodology

2.3.1. Triacylglycerol composition

Triacylglycerol composition was measured based on AOCS CE 5-86 (2004) methodology, determined by an Agilent capillary gas chromatography system, Series 6850, with flame ionisation detector (FID), and an Agilent DB-17 capillary column (50% phenylmethylpolysiloxane; length 15 m, internal diameter 0.25 mm and 0.15 µm film thickness). Flow rate was 1.0 ml/min, linear velocity of 40 cm/s, with a detector temperature of 375 °C, injector temperature of 360 °C, oven temperature from 250 to 350 °C (5 °C/min), followed by 350 °C for 20 min, carrier gas of helium; injected volume of 1.0 µl with 1:100 split. Retention times were determined comparing with commercial standards, samples and others vegetable oils (palm oil, soybean oil, and palm kernel oil) previously identified and quantified in our laboratory. All fractions of triacylglycerols in palm oil were quantified based on relative peak area, in duplicate. The results were compared with those obtained following the procedure of Antoniosi Filho, Mendes, and Lanças (1995) and with a literature compilation (Andrikopoulos, 2002).

2.3.2. Fatty acid composition of the monoacylglycerols

Fatty acid composition was determined in duplicate by an Agilent capillary gas chromatography system, Series 6850, FID detector, with an Agilent DB-23 capillary column (50% cyanopropylmethylpolysiloxane; length 60 m, internal diameter 0.25 mm and 0.2 µm film thickness). Flow rate was 1.0 ml/min, linear velocity of 24 cm/s, with a detector temperature of 280 °C, injector temperature of 250 °C, oven temperature: 110 °C for 5 min, 110–215 °C (5 °C/min), 215 °C for 34 min, helium carrier gas; injected volume of 1.0 µl, 1:50 split. Methylation reaction was done using NH₄Cl in methanol solution. In fatty acid methyl esters (FAME) separation saturated salt solution and petroleum ether were used according to the methodology proposed by Hartman and Lago (1973). FAME in petroleum ether were transferred into vials and analysis was done in duplicate. Individual components were identified by comparison with commercial FAMES standards, and other FAMES from vegetable oils (palm oil, soybean oil, and palm kernel oil) prepared, identified and quantified in laboratory previously. Fatty acids were quantified based on relative peak areas.

2.3.3. Isothermal crystallisation

The samples were melted in an oven and kept in an incubator for 15 min at 100 °C to ensure destruction of the crystalline forms. After removing from the oven, the samples were placed in a dry static thermal bath with the temperature controlled by a Duratech tcon Peltier system (temperature range from –5 to 70 °C) at a temperature of 70 °C for 1 h (Campos, 2005). After this period, they were subjected to a temperature of 25 °C and readings of the solids contents taken every 60 s, using low-resolution magnetic pulsed nuclear resonance equipment (NMR) (Minispeq mq 20, Bruker; Silberstreifen, Rheinstetten, Germany), until the solids level became stable.

2.3.4. Differential scanning calorimetry

The equipment used was a Perkin-Elmer Delta Series Model DSC 7 differential scanning calorimeter (DSC) of the power compensation type (Waltham, MA). The samples were previously melted and weighed (about 3–10 mg) in aluminium pans, and covers were sealed into place. An empty sealed aluminium pan was used as reference in the other DSC oven. A baseline was obtained with an empty sealed aluminium pan prior to analysis of samples.

The samples were subjected to the following temperature program: heated to 80 °C and maintained at isothermal conditions for 10 min, cooling to a temperature of –40 °C at a rate of 10 °C/min. DSC values reported are the average of three scans. The manufacturer's software (Pyris Manager 2.04/windows) was used in thermal analysis.

2.3.5. Polarised light microscopy

The samples were melted at 70 °C and a drop transferred onto a glass slide with the aid of a capillary tube. The drop was covered with a pre-heated cover slip before transferring to an incubator at 25 °C and maintaining at this temperature for a period of 20 h. After this period, the slides were transferred to a plate at a temperature of 25 °C (Mettler Toledo, FP82 Microscope Hot Stage). With the aid of a polarised light microscope (Olympus, model BX 50) connected to a digital video camera (Media Cybernetics), images were taken from three different visual fields at a magnification of $\times 40$, and then a single image selected for the analysis (Gamboa & Gioielli, 2006). The Image-Pro Plus software, Version 4.5.1.22 (Media Cybernetics) was used to take the images and carry out the quantitative analysis of the results. The analysis parameter chosen was the maximum diameter of the crystal (greatest length on a given axis).

2.3.6. X-ray diffraction

The crystalline polymorphic form of palm oil was determined according to the AOCS Cj 2-95 (2004) method. The tests were performed in a Philips (PW1710) diffractometer; Bragg-Bretano geometry (0:20); Cu K α radiation ($\lambda = 1.54056$ Å, at 40 kV and 30 mA). The measurements were performed with a 0.02° step in 2θ , with an acquisition time of 2 s, over the range from 5° to 40° (2θ scale). Diffraction was performed at a temperature of 20 °C, sufficient to ensure crystallinity of the samples. The crystalline forms were identified from their characteristic short spacing, calculated using the Bragg Law:

$$\lambda = 2d \sin \theta \quad (1)$$

where λ is the wavelength of the X-ray emitted, d is the short spacing and θ is the angle of diffraction. The α -form is characterised by a single line of diffraction at 4.15 Å. The β' -form is characterised by two lines of diffraction at 3.8 and 4.2 Å or 4.27, 3.97 and 3.71 Å or 3.9 and 4.3 Å. The β -form is associated with a number of diffraction lines, predominantly at 4.6 Å, and lines of lower intensity, including those at 3.9 and 3.8 Å. The sub- β -form may be characterised by a strong peak for a short spacing of 4.73 Å or three intermediate peaks at 4.5, 3.9 and 3.6 Å (AOCS, 2004; Cerdeira, Martini, Candal, & Herrera, 2006; D'Souza, deMan, & deMan, 1990; Yap, de Man, & de Man, 1989). The β - and β' -form contents in the samples were estimated by the relative intensity of the short spacing (AOCS, 2004; Che Man, Shamsi, Yusoff, & Jinap, 2003; Szydłowska-Czerniak, Karlovits, Lach, & Szlyk, 2005).

2.3.7. Statistical analysis

DSC data were statistically analysed by one-way analysis of variance (ANOVA) with Statistica (V.6) Software (Statsoft Inc., Tulsa, OK) Software. Tukey test was applied to determine significant differences between means, at a level of $p < 0.05$.

3. Results and discussion

3.1. Triacylglycerol composition

The triacylglycerol composition of the palm oil was 9.7 ± 0.22 , 50.2 ± 0.6 , 35.7 ± 0.49 and $4.3\% \pm 0.14$ of trisaturated, disaturated–monounsaturated, monosaturated–diunsaturated and triunsaturated

fractions, respectively. The tripalmitin content was $8.5\% \pm 0.11$.

3.2. Fatty acid characterisation of the monoacylglycerols

The monoacylglycerol samples were characterised in relation to their fatty acid compositions. The primary fatty acids of the MP sample were C16:0 and C18:0, in proportions of 45.4 ± 0.05 and $53.6\% \pm 0.05$, respectively. In turn, the MBe sample contained the fatty acids C18:0, C20:0 and C:22:0, with respective percentages of 3.6 ± 0.01 , 6.9 ± 0.01 and $85.5\% \pm 0.02$.

3.3. Crystallisation kinetics

As can be seen in Fig. 1, the induction time was reduced from 33 to 15 and 12 min, respectively, for Po, PoTp1 and PoTp2, suggesting an increase in the crystallisation rate of the samples with added tripalmitin.

The crystallisation behaviour of palm oil was changed by the addition of tripalmitin, a triacylglycerol present in significant amounts in some oils and in the stearin fraction of some fractionated oils, causing anticipation of its crystallisation when subjected to an isothermal condition.

The addition of 1% of monoacylglycerol to palm oil showed a significant effect in reducing the induction time, as shown in Fig. 1. The induction times decreased from 33 to 19 and 13 min, respectively, for PoMp and PoMBe. The addition of MBe to Po showed a greater decrease in induction time than when the same proportion of MP was added.

Monoacylglycerols act as crystallisation inducers, serving as a nucleation seed and consequently facilitating aggregation of the triacylglycerol molecules, thus reducing the induction process time. The presence of these partial acylglycerols did not lead to significant changes in the final solids content after isothermal crystallisation, which is in agreement with the results obtained by Wright, Hartel, Narine, and Marangoni (2000), who found that acceleration of the crystallisation speed by the presence of minor compounds did not necessarily affect the final solid fat content in an isothermal process.

In a study of the interaction of partial acylglycerols and triacylglycerols in milk fat, Foubert et al. (2004) reported two mechanisms of interaction with the triacylglycerol crystals. The first resulted in slower crystal growth, due to competition in binding with the triacylglycerols. The second form involved organisation in a micellar structure of partial acylglycerols, acting as nucleation facilitators, as described by Savage and Dimick (1995) and Skoda and Van de Tempel (1967), reducing the induction time and increasing the number of crystalline nuclei.

The addition of higher levels of monostearin to milk fat accelerated the crystallisation process at lower temperatures, while lower levels associated with higher temperatures delayed the crystallisation process. Distearin provoked a general delay in the crystallisation process. On the other hand, higher levels of monoolein and diolein increased the crystal growth speed, resulting in a less pronounced effect on the induction time (Foubert et al., 2004).

In a study carried out by Niiya, Maruyama, Imamura, Okada, and Matsumoto (1973) with hydrogenated fat, increases in the crystallisation rate, melting point and solid fat content were reported with the addition of saturated monoacylglycerols, such as monopalmitin, monostearin and monobehenin, the effect of the latter predominating over the others in causing rises in the melting point and solids content.

Monoacylglycerol behenic acids are probably more effective as crystallisation inducers, due to the presence of a longer fatty acid chain than those found in high proportions in the monoacylglycerols of the fully hydrogenated palm oil (palmitic and stearic acids),

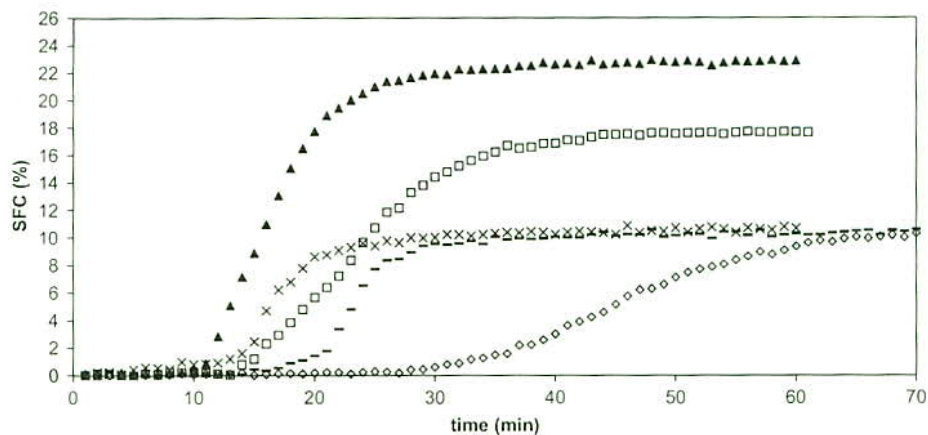


Fig. 1. Isothermal crystallisation of refined palm oil, refined palm oil with added tripalmitin and refined palm oil with added monoacylglycerols at 25 °C: (◇) Po; (□) PoTp1, (▲) PoTp2, (–) PoMp, and (×) PoMBe.

leading to greater stability at the crystallisation seed-forming temperature.

3.4. Thermal behaviour

The results of one-way analysis of variance (ANOVA) indicated that, for the Po sample, the addition of tripalmitin and monoacylglycerols changed significantly the beginning of the crystallisation process (T_{onset}), the temperature at which the exothermal effect is maximum (T_{peak}) and the energy released by the crystallisation process (enthalpy) on the stearin fraction. No significant differences were observed comparing PoTp1 and PoMp, with respect to T_{onset} . In the same way, PoTp1 and PoMBe did not show significant differences concerning T_{peak} .

Fig. 2 shows two distinct exothermic peaks during the crystallisation process of the Po sample. The first, located in the region of higher temperatures, between 31 and 15 °C in the different thermograms, represented the crystallisation phase rich in saturated

triacylglycerols, the stearin fraction. The second, between 10 and –12 °C, represented the crystallisation process of the phase rich in unsaturated triacylglycerols, the olein fraction, which corroborates the observations of Tan and Che Man (2000), who described the formation of two distinct peaks in the DSC analysis of palm oil.

Acceleration of the crystallisation process in the samples with added tripalmitin and monoacylglycerols may be observed by the displacement of the T_{onset} and the T_{peak} , referring to stearin in the region of higher temperatures. As can be seen in Table 1, the start of crystallisation of the Po was early in proportion to the addition of tripalmitin. The presence of MBe resulted in a greater change in the Po crystallisation temperature, by 2.9 °C, whereas with MP it was only by 1.6 °C.

Increasing the crystallisation temperature by the addition of PPP is in agreement with the results of studies by Che Man, Haryati, Ghazali, and Asbi (1999) on the thermal behaviour of crude palm oil and its derivatives, in which the crystallisation peaks of the compounds containing more saturated triacylglycerols moved

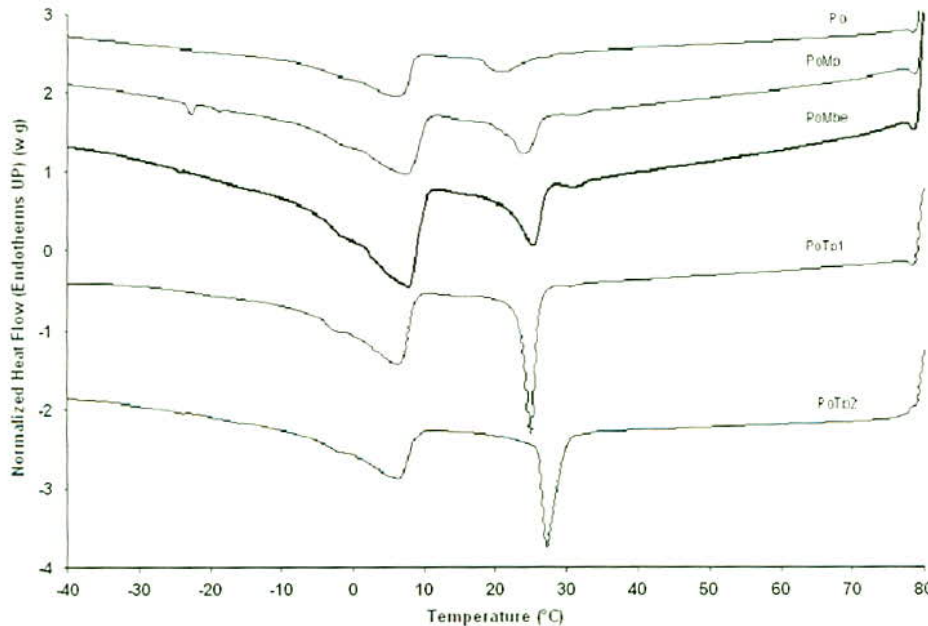


Fig. 2. Thermogram crystallisation of refined palm oil, refined palm oil with added tripalmitin and refined palm oil with added monoacylglycerols: Po; PoTp1; PoTp2; PoMp; PoMBe.

Table 1

Crystallisation temperatures and exothermic peaks of refined palm oil and its blends with tripalmitin and monoacylglycerols.

	Po	PoTp1	PoTp2	PoMP	PoMBe
T_{onset} (°C)	24.37 ± 0.31	25.83 ± 0.06	29.71 ± 0.14	26.00 ± 0.44	27.3 ± 0.36
T_{peak} (°C)	20.17 ± 0.81	24.80 ± 0.00	27.41 ± 0.19	23.63 ± 0.35	25.03 ± 0.21
Area (J/g)	3.99 ± 0.42	19.3 ± 0.03	23.08 ± 0.38	8.73 ± 0.23	13.10 ± 0.26

to the region of higher temperatures. According to Toro-Vazquez, Briceno-Montelongo, Dibildox-Alvarado, Charo-Alonso, and Reys-Hernandez (2000), who studied the crystallisation kinetics of palm stearin in sesame oil, the tripalmitin was primarily responsible for increasing the crystallisation temperature of this blend.

Samples with added tripalmitin led to the release of more heat during the crystallisation of the phase rich in saturated triacylglycerols. On the other hand, the addition of monoacylglycerols in spite of increasing the crystallisation temperature produced a lower increase in the release of energy during the crystallisation process relative to tripalmitin (Table 1). A great increase in the release of heat during the crystallisation process may be detrimental, since it may result in elevated temperatures that will cause the dissolution of already-formed crystals. Wassell and Young (2007) mentioned the addition of small amounts (1–2%) of saturated triacylglycerols as a cheap and effective alternative to induce the start of the crystallisation process.

3.5. Crystalline morphology and microstructure

The minimum and maximum values for maximum crystal diameter at 25 °C were 53 and 128, 55 and 142, 56 and 118, 7 and 99, and 25 and 51 µm, respectively, for Po, PoTp1, PoTp2, PoMP and PoMBe.

It can be seen that the minimum values for the crystal diameter of Po, PoTp1 and PoTp2 were very close to 50 µm, indicating that raising the PPP level did not cause an increase in the smallest crystal diameter formed in palm oil. Higher PPP levels led to the formation of larger amounts of crystals with relatively homogeneous size and form. A small number of clusters can be observed in PoTp2 (Fig. 3).

It can be seen from the Po, PoMP and PoMBe samples that the addition of monoacylglycerols induced the formation of large numbers of small crystalline nuclei, in agreement with that described by Foubert et al. (2004) who reported an increase in the amount of crystallisation seed and in the number of crystals formed and a decrease in the induction period, due to the influence of existing partial acylglycerols. The minimum diameter values, 7 and 25 µm, were much lower than those obtained for Po in the absence of monoacylglycerols.

Monoacylglycerols play the role of crystallisation seeds, dispersed in the palm oil. Triacylglycerol molecules are adsorbed onto the surface of these structures and then the crystallisation process begins. A large number of seeds results in smaller crystals, since the triacylglycerols are distributed during their adsorption and crystallisation.

As seen in Fig. 3, the addition of monoacylglycerols of behenic acid resulted in the formation of a structured network composed of clusters of homogeneous crystals. However, the presence of palm-based monoacylglycerols, while increasing the amount of crystals, did not lead to the formation of a structured network, showing great diversity in their diameter.

The crystallisation occurring from the formation of a large number of small crystalline nuclei could be one of the causes of the lower energy release during this process, since the samples showing lower exothermic peaks during the process possessed the smallest crystal diameters. The energy released during the forma-

tion of larger crystals seems to be greater than that released during the formation of smaller crystals, even when in significantly larger numbers.

The addition of saturated monoacylglycerols leads to the formation of a greater number of crystallisation seeds, possibly more stable to the effect of temperature. During the crystallisation process, a crystalline network is formed that allows for greater interaction between triacylglycerol molecules, between which intermolecular attractive forces such as the Van der Waal's forces can act, which may promote greater intermolecular attraction, leading to a decrease in system solubility, more evident at high temperatures, contributing to the crystallisation process.

3.6. Avrami model

The Avrami model is the one most commonly used to study the crystallisation of fats and may be used to assess the crystallisation kinetics and suggest the nature of crystal growth. The model takes into account that crystallisation occurs by nucleation and by crystal growth and is based on the isothermal transformation conditions, random spatial growth and the kinetics of the system, in which the growth speed of the new phase depends solely on temperature. The Avrami equation is presented in the following way:

$$\frac{SFC}{SFC_{\text{max}}} = 1 - e^{-kt^n} \quad (2)$$

where n is the Avrami exponent (dimensionless), k is the Avrami constant, SFC is the solids content at a given time and SFC_{max} is the maximum level of solids at a given temperature.

The half life of crystallisation, $t_{1/2}$, reflects the magnitude of k and n according to the equation:

$$t_{(1/2)} = \left(\frac{\ln 2}{k} \right)^{1/n} \quad (3)$$

The constant k represents the rate of crystallisation, while the exponent n , known as the crystallisation index, indicates the mechanism of crystal growth. The parameter n is a combination function of a time-dependent nucleation and number of potential growth dimensions (Marangoni, 2005).

Nucleation may be sporadic or instantaneous and crystal growth may be one, two- or three-dimensional, characterising the formation of needles, disks or spherulites, respectively, as the crystalline forms. Values of $n = 3$ correspond to an instantaneous or sporadic nucleation spherulite form or to a sporadic nucleation disk form, while values of $n = 2$ correspond to the sporadic growth of needle-like forms or the instantaneous nucleation of disk-like growth. Although n should be a whole number, fractional values are commonly obtained. This event is primarily related to the formation of crystals with similar morphology from different types of nucleation (sporadic or instantaneous). Fractional values of the exponent n may be explained by the simultaneous development of crystals with different morphologies (Marangoni, 2005).

The parameters of the Avrami model were calculated based on the results from isothermal crystallisation at 25 °C, considering the time interval occurring when the induction period ends, up to 10 min after stabilisation of the solid fat content.

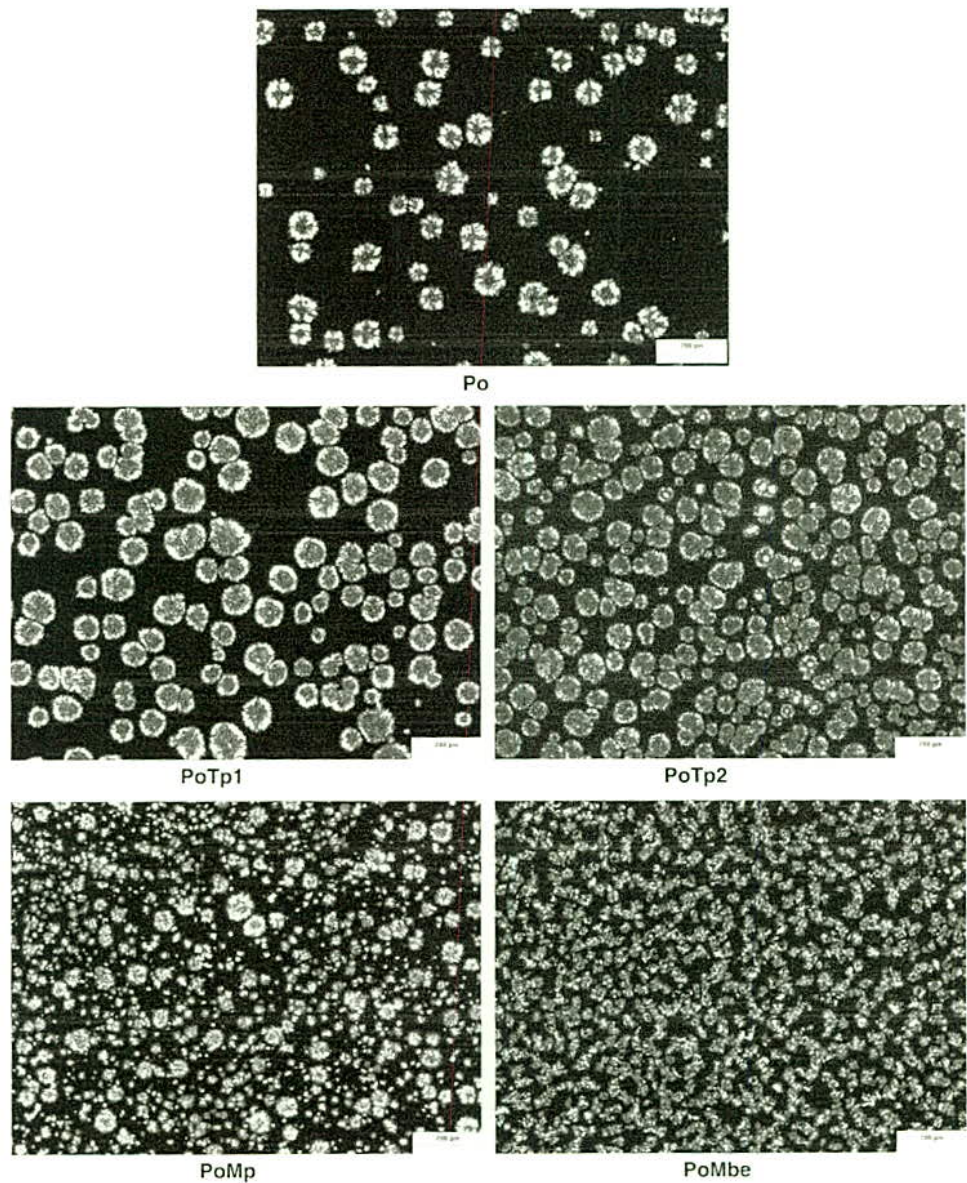


Fig. 3. Microscopic images under polarised light at 25 °C of refined palm oil, refined palm oil with added tripalmitin and refined palm oil with added monoacylglycerols: Po; PoTp1; PoTp2; PoMp; PoMBe. The bar represents 200 μm.

From the *k*-values reported in Table 2, it can be observed that the crystallisation rates increase with the percentage of PPP. Of the samples with added monoacylglycerols, PoMBe showed higher crystallisation rates than PoMp, confirming the greater effectiveness of the monoacylglycerols of behenic acid as accelerators of the crystallisation process, as compared to palm-based monoacylglycerols. Both the samples with added tripalmitin and with added monoacylglycerols showed higher rates of crystallisation than Po.

Table 2
Avrami model parameters for the crystallisation of refined palm oil and its blends with tripalmitin and monoacylglycerols at 25 °C.

	Po	PoTp1	PoTp2	PoMP	PoMBe
<i>k</i> (min ^{−n})	1.72E−07	4.60E−05	8.91E−04	1.41E−06	4.05E−04
<i>n</i>	3.9	3.0	2.4	4.1	2.6
<i>R</i> ²	0.96	0.96	0.90	0.81	0.81
<i>t</i> _{1/2}	48.8	24.4	16.5	24.8	18.0

These results agree with those found for the value of the half life of crystallisation.

From the exponent *n*, observed in Table 2, a tendency for crystal formation of the spherulite type for Po can be noticed. The addition of 1% of palm-based monoacylglycerols did not change the crystal morphology, since crystals of the spherulite type continued to form. Although the *n*-value obtained for PoTp2 was 2.4, Fig. 3 shows the formation of spherulites. For PoTp2 and PoMBe, the *n*-values suggest a transition from two-dimensional growth, disc type, to three-dimensional growth, spherulite type.

3.7. Crystalline polymorphism

From the X-ray diffractograms in Fig. 4, the absence of peaks for a short spacing of 4.6 Å and the presence of an intense peak showing crystals with a short spacing of 4.2 Å can be seen for Po, where crystals with a short spacing of 3.8 Å can also be observed. This configuration characterises the absence of β-crystals and the

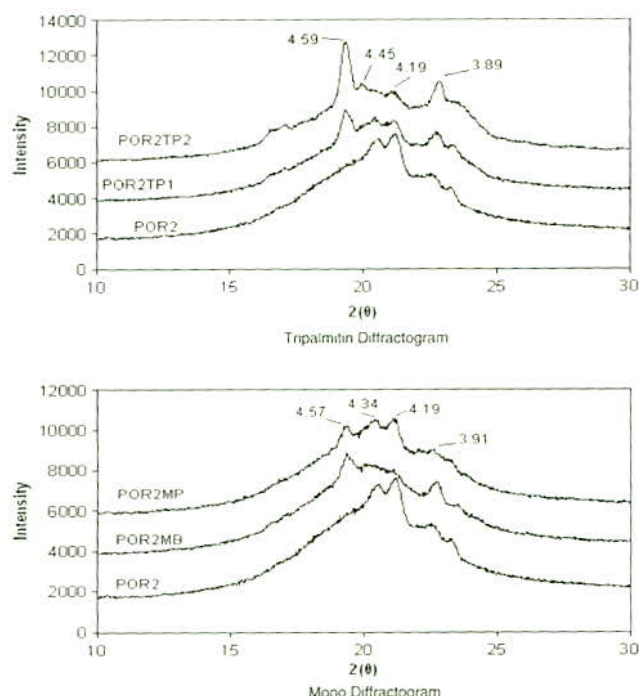


Fig. 4. Diffractograms of refined palm oil, refined palm oil with added tripalmitin and refined palm oil with added monoacylglycerols at 20 °C: Po; PoTp1; PoTp2; PoMp; PoMBe.

strong presence of β' crystals. In a similar way, Braipson-Danthine and Gibon (2007) demonstrated the diffraction lines of the β' -form for palm oil at 20 °C, with peaks of low intensity suggesting short spacings of 4.32 and 4.12 Å and peaks of high intensity in the short spacings of 3.88 and 4.20 Å, close to those obtained in the present paper.

The addition of tripalmitin induced the formation of polymorphic β -form crystals, and the amount of β -crystals formed was in proportion to the addition of tripalmitin, as can be seen from the increase in intensity of the diffraction peak for a short spacing of 4.6 Å, characteristic of PoTp1 to PoTp2.

The addition of monoacylglycerols also led to a change in the polymorphic form of the crystals present in palm oil. The presence of MP led to the formation of β -type crystals. When MBe was added, peaks for β -crystals appeared and a sub- β transitional form could also be observed, indicated by short spacings of, respectively, 4.6 and 3.9 Å. Adding 1% of fully hydrogenated palm-based monoacylglycerols also caused the formation of β -crystals, despite coexisting with a higher content of β' -crystals, since a relatively intense peak for a short spacing of 4.2 Å can be observed.

The decreasing intensity of the peaks related to the β' -form and simultaneous increase in the intensity of the β peaks and appearance and increase in intensity of peaks related to a transition of the sub- β form, indicated by, respectively, short spacings of 4.5 and 3.9 Å, shows the effect of PPP in facilitating the transition to β .

Mazzanti, Guthrie, Sirota, Marangoni, and Idziak (2004) reported that the formation of the β -phase was largely dependent on a previously formed α -phase. The polar lipids (acylglycerols) act as crystallisation sites for the induction of crystallisation in the initial α -phase. From this previously formed α -stage, the triacylglycerols could switch to a β -phase, due to increased stability of the crystalline arrangement. However, the absence of polar lipids allows for freer accommodation of the triacylglycerol molecules in the β' -form, inducing a quick transition from the α to the β' -form.

Smith, Furó, and Smith (2007) described the action of partial acylglycerols in the modification of crystal morphology, by binding them to a crystalline face and preventing deposition of triacylglycerol molecules on that surface, reducing crystalline growth in this region. Wright and Marangoni (2003) also stated that when impurities were present in a fat crystal, they generally modified the growth of certain faces, changing the morphology of the crystalline structures. Even so, the authors found no changes in the crystalline morphology of milk fat due to the removal of minor compounds or the addition of diacylglycerols.

Timms (1984) relates the β' -form to the asymmetry of the triacylglycerol molecule in the presence of saturated and unsaturated fatty acids. Similarly, the β -form is related to the symmetry of triacylglycerols, both in the occupancy of the 1,3 positions and in the occupancy of all three positions by fatty acids of similar structures. This statement confirms the increase in the polymorphic β -form and the decline in β' with the addition of tripalmitin, a completely symmetrical triacylglycerol.

Monoacylglycerols of fully hydrogenated palm oil favoured the formation of β -crystals without leading to the removal of β' -crystals, which makes it an important inducer of the crystallisation process of fats in the food industry. Nevertheless, the addition of tripalmitin and monoacylglycerols of behenic acid as accelerators of the crystallisation process of palm oil, leading to β -crystal formation, may be very important in the chocolate industry, where this type of crystal is desired.

4. Conclusions

The palm oil crystallisation process may be changed by adding tripalmitin and monoacylglycerols. The addition of tripalmitin heightened the speed of crystallisation, the increase in solids content, the release of thermal energy, the increase in size of the triacylglycerol crystals and the formation of β -crystals. In turn, the addition of monoacylglycerols accelerated the crystallisation of palm oil by increasing the number of crystallisation seeds, reducing the size of the crystals formed and favouring the formation of β -crystals, without changing the solid fat content at the end of the crystallisation process.

The addition of saturated monoacylglycerols and triacylglycerols affected the crystallisation of palm oil, and by controlling these modifications, its application in specific processes could become possible. Alteration of its polymorphism, favouring the production of β -crystals instead of the β' -type, could make its application in the chocolate industry possible, decreasing production costs without modifying the characteristics of the final product. Higher crystallisation rates decrease process costs and would make it possible to use this oil in the production of food that requires high rates of crystallisation, such as candy coatings and cookie fillings, conserving the desired palm oil characteristics such as its plasticity.

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Review

New and Existing Oils and Fats Used in Products with Reduced *Trans*-Fatty Acid Content

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ABSTRACT

The US Food and Drug Administration's final ruling on *trans*-fatty acid labeling issued in 2003 has caused a rapid transformation in the fat and oil industries. Novel ingredients and improved technologies are emerging to replace partially hydrogenated fats in foods. We present an overview of the structure and formation of *trans* fatty acids in foods, and a comprehensive review of the newly formulated products and current procedures practiced by the edible oil industry to reduce or eliminate *trans* fatty acids in response to the Food and Drug Administration's regulations mandating *trans* fat labeling of foods.

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T*rans*-fatty acid (TFA) intake has been convincingly associated with risk of heart disease based on epidemiologic and clinical studies (1-27). There has been concern about the safety of TFA since partially hydrogenated oils were established as alternatives to lard and butter in processed foods (28). Whereas initial human feeding studies suggested TFA did not adversely affect plasma total cholesterol levels in individuals fed formula diets containing partially hydrogenated oils (29,30), in one of these studies serum lipoprotein profiles were not evaluated (29). In another study it was found there was no change in serum lipoprotein profiles due to TFA in the experimental diets (30). However, results of later investigations conflicted with these early findings. Mensink and Katan (14) investigated the effect of TFA compared to saturated fatty acids (SFA) and *cis*-monounsaturated fatty acids (oleic acid) on serum low-density lipoprotein (LDL) and high-density lipoprotein (HDL) cholesterol levels in individuals fed natural mixed diets

containing 10% of energy intake as any of those fats. Their results indicated that TFA had as many unfavorable effects on serum lipoprotein profiles as SFA, because TFA increased LDL cholesterol levels but also decreased HDL cholesterol levels.

Concerned about health issues regarding TFA, the US Food and Drug Administration (FDA) requested the Food and Nutrition Board of the Institute of Medicine to prepare a report on TFA to assist in their consideration of a citizen petition for *trans*-fat labeling of foods (15). Possible adverse effects of TFA cited in this report included changes in blood lipid concentrations, with numerous studies indicating an increase in total cholesterol and LDL cholesterol levels. There was also concern about the potential effect of high TFA intake on individuals with elevated concentrations of lipoprotein a (15). Numerous population-based prospective studies as well as controlled feeding trials were cited in this publication.

Compelling data linking dietary TFA to increased risk of coronary heart disease (CHD) originated from large, population-based prospective studies, comprising 667 to 80,082 men and women in different age groups, monitored for 6 to 20 years (1,5,6,8,9) as well as controlled feeding trials. Among these studies are the US Health Professional's Follow-Up Study (1), the Finnish Alpha-Tocopherol, Beta-Carotene Cancer Prevention Study (8), the US Nurse's Health Study 14-year and 20-year follow-up (6,9), and the Dutch Zutphen Elderly Study (5). These studies were consistent in finding a positive strong association between TFA intake and risk of CHD. Interestingly, a weaker correlation between SFA intake and risk of CHD was reported (1,6,8,9). For instance, the Nurse's Health Study (6) estimated that replacement of 5% of energy from SFA by *cis*-unsaturated fats would reduce CHD risk by 42%, whereas substitution of 2% of energy from TFA by *cis*-unsaturated fat would result in a 53% reduction in CHD risk. These data suggested that small decreases of TFA in the diet would most likely produce a large reduction in CHD risk (6,12). The increased CHD risk related to TFA consumption predicted by these studies can be partly explained by the adverse effects of TFA on blood lipid profiles. Controlled feeding trials have shown that TFA intake compared to *cis*-unsaturated fat increases LDL cholesterol and decreases HDL cholesterol levels, which consequently increases the total cholesterol/HDL cholesterol ratio (2,14,16-23), a predictor of CHD risk. Also, TFA raise levels of lipoprotein a, which has been associated with increased risk for cardiovascular and cerebrovascular disease (15,24). In addition, TFA raise plasma triglyceride concentrations, another marker of CHD risk (12,13). Plasma markers of

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systemic inflammation and endothelial dysfunction such as C-reactive protein, tumor necrosis factor receptors, E-selectin, interleukin-6, and vascular cell adhesion molecules, are also unfavorably affected by TFA consumption (10,11,13,25). Other studies have shown that TFA competes with essential *cis*-fatty acids by inhibiting their incorporation into membrane phospholipids, and interfere with n-3 and n-6 fatty acid metabolism, eicosanoid biosynthesis, and prostaglandin balance that in turn may trigger thrombogenesis (12,26,27). High TFA intake has also been linked to insulin resistance (12).

Based on analytical data for individual fatty acids generated by Enig and colleagues (31,32) and by Slover and colleagues (31,33), and US Department of Agriculture (USDA) production and sales figures of commodity foods, the average TFA intake of the US population by 1983 was estimated to be 8 g/day per capita, with 85% coming from foods containing partially hydrogenated oils and the rest from meat and dairy products. In 1999 Allison and colleagues (34), using food intake data from the 1989-1991 USDA Continuing Survey of Food Intakes by Individuals (35) and the TFA content of foods obtained from the 1995 USDA database of TFA content of selected foods (36), calculated the average TFA intake in the United States to be approximately 5.3 g/day per capita, with dietary partially hydrogenated oils remaining the major contributor (80%). More recently, based on the 1994-1996 USDA Continuing Survey of Food Intakes by Individuals (37), the 1995 USDA database of TFA content of selected foods (36), and other data, the FDA has estimated that the average TFA daily intake by US adults is 5.8 g per capita (38). The FDA also assessed TFA consumption by food groups, and reported that products containing partially hydrogenated oils constituted the major source of TFA intake (79.4%). Among foods containing partially hydrogenated oils, main contributors of TFA intake included margarine (16.56%), cakes and related products (23.82%), cookies and crackers (9.78%), fried potatoes (8.32%), chips and snacks (4.81%), and household shortening (4.28%) (38). TFA intake associated with animal products represented just 20.6% (38).

In 1999 the FDA issued a proposal to require that TFA in a serving of food be included in the amount of SFA declared on food labels (39). After public comment and deliberation, in 2003 the FDA issued the final TFA ruling requiring that TFA and SFA be itemized separately (38). Explicitly, the FDA final rule on TFA labeling mandates the declaration of TFA content in the Nutrition Facts label of food products, effective January 1, 2006 (38), with TFA reported in a separate line below SFA. According to the ruling, TFA are defined as "all unsaturated fatty acids that contain one or more isolated double bonds in *trans* configuration," which excludes fatty acids with conjugated double bonds. If the TFA content of a product is equal to or greater than 0.5 g per serving, it must be declared in the Nutrition Facts panel of said product. On the other hand, if the TFA content is below 0.5 g per serving, TFA must be declared as 0 g.

To comply with labeling regulations, the food and edible oil industries face the challenge of accurately analyzing and reporting TFA. In addition, although the required disclosure of TFA content does not include maximum allowable limits, the unhealthful image associated with

TFA has prompted food manufacturers to evaluate their products and seek more healthful alternatives. As the TFA ruling becomes operative, dramatic changes are taking place at the core of long-established edible oil technologies. The outcome will most likely lead to changes in the fatty acid composition of many widely consumed processed food products, such as snack foods and margarines, which have been available for years. The expected reduction in TFA in US foods will result in overall reduction in daily TFA intake, and may contribute to improved health status for the public. In Denmark, for example, consumption of TFA has decreased from 8.5 g/day per capita in 1976 to 2.6 g/day per capita in 1996 (3,31). This decrease in TFA intake may be associated in part with reduced use of table and frying margarines and reduced content of TFA in Danish margarine products (31). Remarkably, during this 20-year period a simultaneous 50% decrease in deaths from CHD has been observed in the Danish population (3).

The purpose of this review is to give a general background on the properties and formation of TFA in foods and to present the evolving technologies and the novel ingredients that the food and edible oil industries are developing to provide products with low to zero TFA content.

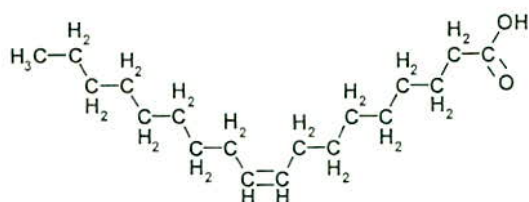
OCCURRENCE OF TFA

With rare exceptions, almost all edible fats and oils of plant origin contain unsaturated fatty acids in the *cis* conformation (40). TFA are found naturally, in low levels, in meat and dairy products as the result of microbial hydrogenation of *cis*-unsaturated fatty acids in the stomach of ruminant animals. However, the major source of TFA is products containing industrially produced partially hydrogenated vegetable oils (40). In addition, small amounts of TFA isomers are found in refined edible oils due to the high temperatures used during the deodorization procedure (41). The Figure illustrates the *cis* and *trans* configuration of double bonds in fatty acids.

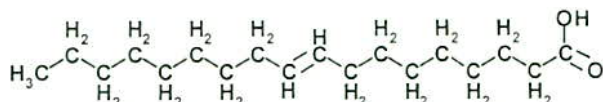
On average, the TFA content in ground beef (36,42), beef tallow* (40,42), butter† (40,42), and whole milk (36) is 1 g/100 g, 5 to 6 g/100 g, 2 to 7 g/100 g, and 0.07 to 0.1 g/100 g, respectively. Partially hydrogenated oils are a key component of margarines, shortenings, frying oils, baked products, confectionery products, deep-fried products, and many processed snack foods (31,36). For example, TFA concentrations reported in shortenings, margarine/spreads, breads/cake products, cookies and crackers, salty snacks, and cake frostings and sweets are 10 to 33

*Concentrations were estimated based on total fat value (grams per 100 g food) of beef tallow obtained from the US Department of Agriculture Nutrient Database, SR18 (No. 04001) (42) and the *trans*-fatty acid content of beef tallow in grams per 100 g total fat (5% to 8%) obtained from reference 40.

†Concentrations were estimated based on total fat value (grams per 100 g food) of salted butter obtained from the USDA Nutrient Database, SR18 (No. 01001) (42) and the *trans*-fatty acid content of butter in grams per 100 g total fat (5% to 8%) obtained from reference 40.



Cis-9-Octadecenoic Acid (*Cis*-9-18:1 or Oleic Acid)



Trans-9-Octadecenoic Acid (*Trans*-9-18:1 or Elaidic Acid)

Figure. Chemical structures of *cis*- and *trans*-9-octadecenoic acid (18:1).

g/100 g, 3 to 26 g/100 g, 0.1 to 10 g/100 g, 1 to 8 g/100 g, 0 to 4 g/100 g, and 0.1 to 7 g/100 g, respectively (36,43)[‡].

Vegetable oils have a high content of polyunsaturated fatty acids (eg, linoleic and linolenic acids) and are prone to oxidation. Industrial hydrogenation is performed to increase the stability, resistance to oxidation, and shelf life of the oil. In addition, hydrogenation raises the melting point of unsaturated vegetable oils, which are liquid at room temperature, converting them into solid/semi-solid fats (40,41,44,45) suitable for products such as shortenings and margarines for which a solid fat structure is essential.

PRODUCTION AND PROPERTIES OF PARTIALLY HYDROGENATED VEGETABLE OILS

Based on work done by the French chemist Paul Sabatier on the metal-catalyzed hydrogenation of unsaturated organic compounds, German chemist Wilhelm Normann developed the method for hydrogenation of edible oils in 1903 (44). Chemically, the hydrogenation of oils is the reduction of the double bonds in unsaturated fatty acids to single saturated bonds, by the reaction of hydrogen gas in the presence of a metal catalyst. The metal catalyst used at the time was nickel, and it has practically remained the same in the current hydrogenation procedures (41). Complete reduction of all double bonds in the oil would yield 100% SFA, whereas reduction of only a fraction of the double bonds results in partially hydrogenated fats. During the process of hydrogenation, due to the reaction mechanisms, the *cis* double bond can open up

[‡]Trans-fatty acid values from reference 43 were converted from trans fatty acid grams per serving to grams per 100 g food.

and reform into a *trans* double bond, as well as shift positions along the fatty acid carbon chain. By adjustment of the hydrogenation reaction parameters, such as catalyst concentration, hydrogen pressure, temperature, and agitation, the production of *trans* double bonds can be modulated. For example, maximum formation of TFA isomers is achieved at low hydrogen pressures (100 to 200 kilopascal [kPa]), high temperatures (200°C to 215°C), and a catalyst concentration of 0.005% nickel/oil. Whereas lower formation of TFA isomers (but higher conversion of the double bonds to saturated bonds) is achieved at higher hydrogen pressures (300 kPa), lower temperatures (165°C to 180°C), and slightly higher catalyst concentrations (0.008% nickel/oil) (41).

The TFA content of partially hydrogenated oil can range from 10 to 60 g/100 g, with 25 to 45 g/100 g being the most frequent concentration (41). By comparison, the concentration of TFA in ruminant fats (eg, beef tallow and butter) is 5 to 8 g/100 g (40,41), and up to 3 g/100 g in refined edible oils (41).

Structurally, *cis* double bonds in unsaturated fatty acids produce a bend in the chain that prevents unsaturated fatty acids from packing as tightly as SFA (see the Figure). As a consequence, a *cis* unsaturated fatty acid has a lower melting point than a SFA with the same molecular weight. Conversely, the *trans* double bonds do not create a bend on the fatty acid chain. Therefore, *trans* unsaturated fatty acid chains are virtually straight, resembling SFA, and display higher melting points than the corresponding *cis* isomers.

INDUSTRIAL USE OF PARTIALLY HYDROGENATED VEGETABLE OILS

The patent for the technology to produce partially hydrogenated oil was acquired by the British company Joseph Crossfield and Sons, establishing the manufacture of partially hydrogenated oil in Europe around 1906 (44). Partially hydrogenated oils were introduced in the US food supply in 1911 when Procter and Gamble (Cincinnati, OH), after obtaining rights to the patent, launched Crisco shortening, made of partially hydrogenated cottonseed oil. However, partially hydrogenated oils were not extensively used in the United States until 1950, when the food industry became interested in manufacturing margarines out of partially hydrogenated oil (45). Margarines based on partially hydrogenated oil were less expensive to produce, and had higher melting points, longer shelf life, and improved organoleptic properties compared to butter or lard. By the 1970s margarine sales doubled those of butter, mainly because research at the time indicated that SFA and cholesterol were linked to heart disease, and butter and lard are major dietary sources of SFA and cholesterol. As a result, partially hydrogenated oil replaced butter and lard in numerous products, including baked goods, shortenings, confectionery, and deep-fried foods (45).

ALTERNATIVES TO PARTIALLY HYDROGENATED VEGETABLE OILS

With the TFA labeling requirement in place, the food and edible oil industries have been motivated to explore al-

alternatives to TFA in their products. Technically, reformulation of the fats to exclude TFA and simultaneously preserve the structural and palatable characteristics of the food product (eg, mouth-feel, plasticity, and flavor), and minor undesirable effects in health, is not an easy task. In addition, some manufacturers have sought to offer TFA alternatives that have a targeted fatty acid profile aside from simply zero TFA. A number of technologies have been developed and are currently in use by the food and edible oil industries in products with minimal to zero TFA content (46-52), including:

• Modification of the chemical hydrogenation process to produce partially hydrogenated fats with low TFA content.

• Selection of oil seeds with modified fatty acid composition through plant breeding and genetic engineering techniques.

- Use of tropical oils (eg, palm oils, palm kernel oil, and coconut oil) and fractionated tropical oils.
- Interesterification of mixed fats.

Some of these technologies have been available to the food industry for some time; however, for a number of reasons, including cost and technical challenges, the industry did not fully embrace them when they were created. In fact, TFA reductions in ingredient type foods such as oils, shortenings, and margarines started in the mid 1990s; however, with the TFA labeling requirement, there has been more incentive for multi-ingredient manufacturers to incorporate the lower TFA fats into their products. For example, the average fat content of US margarines decreased from 80 g/100 g in 1980 to 40 to 70 g/100 g by 2000 (53,54) in response to consumer petitions for lower-fat and lower-energy products. List and colleagues (54) report that the average TFA content of US margarines/spreads was 19.5 g/100g in 1992, decreased to 16.1 g/100 g in 1995, and to 8.8 g/100 g in 1999. Several low- and no-fat margarine-like-spreads were available before 1998, such as Promise, Imperial soft tub, and I Can't Believe It's Not Butter (Unilever Bestfoods North America, Englewood Cliffs, NJ), and Fleischmann's margarine/spread line (ConAgra Foods, Inc, Omaha, NE) (53). In 1998 Unilever Bestfoods North America reformulated their Promise line of regular and low-fat spreads to contain zero TFA, and so did ConAgra Foods, Inc, with their Fleischmann's line of regular and low-fat spreads (53). Therefore, there was a clear effort by the margarine industry to reduce TFA in their products. At the time, there were several published studies comparing the effects of butter and margarines containing TFA on blood lipid profiles (55,56). Judd and colleagues (56), in a controlled feeding study, compared the effects of butter, a market-representative tub-type margarine containing TFA, and a zero *trans*-tub-type margarine high in polyunsaturated fatty acids on the blood lipid and lipoprotein concentrations of 46 subjects. Although consumption of both margarine diets resulted in a lowering of total and LDL cholesterol levels compared with the butter diet, the favorable blood lipid effect was more pronounced with the *trans*-free margarine.

Examples of commercial products based on the technologies enumerated above are summarized in Table 1.

Some of these products were designed to have a favorable fatty acid profile beyond simple elimination of TFA and/or other desirable qualities such as reduced calorie content.

Modification of the Hydrogenation Process

Bunge Oils, Inc (St Louis, MO), has developed a proprietary method to chemically hydrogenate edible oils with the production of less than 10% *trans* isomers during the procedure (57). This new hydrogenation procedure involves the use of a conditioned nickel catalyst that selectively prevents the formation of *trans* stereoisomers. Based on this technology, Bunge is offering to the commercial food industry two low *trans* shortenings and two low *trans* margarines in their Elite product line (58). These products are derived from soybean and cottonseed oils and contain less than 6% TFA (see Table 1).

King and colleagues (59), at the USDA National Center for Agricultural Utilization Research, in Peoria, IL, report a procedure for the hydrogenation of soybean oil in supercritical carbon dioxide, hydrogen, and nickel catalyst with minor formation of *trans* products.

Wright and colleagues (60), at the University of Toronto (Toronto, Ontario, Canada), have also reported a method for the hydrogenation of canola oil using mixed metal catalysts (nickel and palladium) and lower temperatures that promotes the formation of *cis* isomers, and very low production of TFA (11%).

Lalvani and colleagues (61,62) working in the Mechanical Engineering and Energy Processes Department at Southern Illinois University (Carbondale, IL) have designed a promising and innovative process for the hydrogenation of edible oils. The process consists of the electrochemical hydrogenation of oils at low temperature in the presence of formate as electro-catalyst, with nickel and palladium as catalysts. This method is efficient in the production of significant amounts of hydrogenated fatty acids, and the use of low operating temperatures (<70°C) restricts the formation of TFA isomers to less than 10% of the oil content.

Manipulation of Fatty Acid Composition of Edible Oil Seeds Using Conventional Plant Breeding and Genetic Engineering Techniques

Many oil seeds with modified fatty acid composition have been created by both traditional seed breeding procedures and modern genetic methods for the purpose of altering nutritional and/or technical properties of the oil. Plant breeding techniques have been successful in selection of seed mutants expressing higher oil yields and a modified fatty acid composition (63). An example is the virtual elimination of erucic acid, a fatty acid with negative health implications, from rapeseed cultivars destined for edible oil production. These low erucic cultivars are used to produce canola oil, which has become a widely consumed cooking oil (63). Other successful breeding programs have been conducted with oil-producing sunflowers. In Russia from 1910 to the 1960s, sunflower seed varieties were selected that were capable of yielding 40% to 55% oil, as opposed to 30% to 35% oil in the wild type varieties (64). Several of these high oil sunflower varieties were introduced in the United States and Canada in

Table 1. Some examples of oil/fat industry technologies and products for reducing <i>trans</i> -fatty acids (TFA) in foods									
Product	Description	Recommended applications	Fatty Acid Profile						Reference
			TFA (%)	SFA ^a (%)	PUFA ^b (%)	Oleic (%)	Linoleic (%)	Linolenic (%)	
Modification of chemical hydrogenation process									
Elite Vream RighT ^c	Partially hydrogenated shortening from soybean/cottonseed oils	Multiple uses	<6	25-29	NA ^d	NA	NA	NA	58
Elite Vreamay RighT ^c	Partially hydrogenated shortening from soybean/cottonseed oils	Cakes and icings	<6	25-29	NA	NA	NA	NA	58
Elite Victor RighT ^c	Low <i>trans</i> margarine from soybean/cottonseed oils	All purpose margarine	<6	25-29	NA	NA	NA	NA	58
Modification of fatty acid profile of oilseeds by plant breeding or genetic engineering									
Clear Valley/Odyssey mid/high-oleic canola oils ^e	Mid/high-oleic canola oil	High stability oils for industrial frying, baking, and blending with other fats	<1.5	6	NA	65-75	12-22	<3.0	76
Clear Valley/Odyssey high-oleic sunflower oils ^e	High-oleic sunflower oil	High stability oils for industrial frying, baking, and blending with other fats	<1.5	8	NA	79	11	<0.5	76
NuSun ^f	Mid-oleic sunflower oil	High stability oil for industrial frying, baking, and blending with other fats. Contains 66% RDA ^g for vitamin E	Trace	9	NA	65	25	<1.0	77
Natreon canola oil ^h	Mid-oleic canola oil	High stability oils for industrial frying, baking, and blending with other fats	~1	7	18	74	NA	NA	83
Natreon high oleic sunflower oil ^h	High-oleic sunflower oil	High stability oils for industrial frying, baking, and blending with other fats	~1	10	7	>80	NA	NA	83
Trisun ⁱ	High-oleic sunflower oil	High stability oil for industrial frying, baking, and spray coating of cereals and dried fruits	Trace	8	NA	81	9	0.1	84
Nutrium Low Lin soybean oil ^j	Low linolenic soybean oil	High stability oil	0	NA	NA	NA	NA	<3	85
Vistive soybeans ^k	Low linolenic soybeans	NA	0	NA	NA	NA	NA	<3	86
Tropical oils									
Sans Trans 55 ^l	Palm oil bead flake shortening	Dry cake mixes, icing, and heat stabilizer	0	73	NA	NA	NA	NA	88
Sans Trans 50 ^l	Palm oil flake shortening	Structuring fat for icing and bakery dry mixes	0	65	NA	NA	NA	NA	88
Sans Trans 45 ^l	Palm oil plastic shortening	Cookies, crackers	0	55	NA	NA	NA	NA	88
Sans Trans 39 ^l	Palm oil soft plastic shortening	Cakes, vegetable dairy products	0	50	NA	NA	NA	NA	88
Sans Trans Fry ^l	Palm oil soft plastic shortening	Frying	0	55	NA	NA	NA	NA	88
Sans Trans Liquid Fry ^l	Palm oil liquid shortening	Frying	0	45	NA	NA	NA	NA	88
Flake shortenings ^m	Palm and palm kernel oil shortenings	Baked goods (biscuits, cookies, pizza dough)	0	NA	NA	NA	NA	NA	89
Zero-Trans Nutresca APS-96 ⁿ	Palm and palm kernel oil shortening	All-purpose shortening	0	74	3	17	NA	NA	90
Palm Oil 81-20-RBD ⁿ	Refined palm oil	Baking, frying, pasta shortenings, margarines	0.4	47	9	38	NA	NA	90
Nutreolin 64 ⁿ	Prefractionated palm oil with vitamins A and E	Baking, frying, shortenings, coloring agent for margarines	0	43	14	43	NA	NA	90
Nutreolin 70 ⁿ	Prefractionated palm oil with vitamins A and E	Cooking, baking, salad dressings	0	36	14	50	NA	NA	90

(continued)

(continued)

Table 1. Some examples of oil/fat industry technologies and products for reducing *trans*-fatty acids (TFA) in foods (continued)

Product	Description	Recommended applications	Fatty Acid Profile						Reference
			TFA (%)	SFA ^a (%)	PUFA ^b (%)	Oleic (%)	Linoleic (%)	Linolenic (%)	
NovaLipid line ^o	Palm oil, palm kernel oil, coconut oil, palm oleine, palm, stearine-based oils, and shortenings	Ice cream, chocolate coating and filling, margarines, frying, bakery	0	NA	NA	NA	NA	NA	91
Interesterification Novalipid line ^o	Shortenings made from interesterified soybean oil with fully hydrogenated soybean and cottonseed oils	Wide range of baking applications (pastries, cakes, cookies, breads)	<1	NA	NA	NA	NA	NA	91
Benefat Salatrim ^p	Low-energy triglyceride blend, made by interesterification of acetic/propionic/butyric triglycerides (short-chain), with long-chain triglycerides (stearic acid) derived from fully hydrogenated vegetable oil	Reduced-calorie baked products, confectionery, chocolate coating, biscuit filling, nutrition bars	0	33-66	NA	NA	NA	NA	96
Enova ^{oa}	Edible oil with 80% diacylglycerides made by interesterification of soybean/canola oil-derived-unsaturated fatty acids with glycerol	Baking, grilling, frying, salads	0	4	50	36	NA	NA	99
Neobee MCT ^r	Medium-chain triglycerides oils/shortenings made by esterification of a blend of C8 ^s and C10 ^r acids fractionated from coconut and palm kernel oils with glycerol	Nutritional products, carrier for flavors, vitamins, essential oils and color; baking, confectionery, margarines, spreads; coatings of dried fruits; beverages	0	100	0	0	0	0	101
Neobee MLT-B ^r	Shortening made from interesterified medium-chain triglycerides, tristearin, and fully hydrogenated soybean oil	Baking, margarines, coatings, salad oils	0	100 C8: 30% C10: 20% C16 ^u : 25% C18 ^v : 25%	0	0	0	0	101
Vivola ^w	Edible oil made from medium-chain triglycerides, n-3, n-6, and phytosterols	Cooking, baking, and salad dressing	0	65	NA	NA	NA	NA	103
Other fats TransEnd 350 ^o	Soft solid shortening made from high-oleic canola oil and fully hydrogenated cottonseed oil	Cookies, crackers, breads, pizza dough, cake mixes, scones	<2	10-14	NA	NA	NA	NA	76

(continued)

Table 1. Some examples of oil/fat industry technologies and products for reducing *trans*-fatty acids (TFA) in foods (continued)

Product	Description	Recommended applications	Fatty Acid Profile						Reference
			TFA (%)	SFA ^a (%)	PUFA ^b (%)	Oleic (%)	Linoleic (%)	Linolenic (%)	
TransEnd 370 ^c	Shortening made from high-oleic canola oil and fully hydrogenated cottonseed oil	Cookies, biscuits, dough mix, doughnuts	<2	13-17	NA	NA	NA	NA	76
TransEnd 390 ^c	Solid shortening made from high-oleic canola oil and fully hydrogenated cottonseed oil	Pastries, biscuits, pie crusts	<2	18-22	NA	NA	NA	NA	76
Essence ^d	Nonhydrogenated shortening blends	Blending with other oils Cookies, pie crust, cakes, crackers, pizza crust	<1	20-33	NA	NA	NA	NA	90

^aSFA=saturated fatty acids.
^bPUFA=polyunsaturated fatty acids.
^cBunge Oils Inc (St Louis, MO).
^dNA=not available.
^eCargill Inc (Minneapolis, MN).
^fNational Sunflower Association (Bismarck, ND).
^gRDA=Recommended Dietary Allowance.
^hDow AgroSciences (Indianapolis, IN).
ⁱHumko Oil Products (Cordova, TN).
^jDupont (Wilmington, DE) and Bunge Oils Inc (St Louis, MO).
^kMonsanto Co (St Louis, MO).
^lLoders Crocklaan (Channahon, IL).
^mGolden Foods (Louisville, KY).
ⁿAarhus United (Port Newark, NJ).
^oADM (Decatur, IL).
^pDanisco (Denmark).
^qKao Corp (Tokyo, Japan).
^rStepan Co (Northfield, IL).
^sC8=caprylic acid.
^tC10=capric acid.
^uC16=palmitic acid.
^vC18=stearic acid.
^wForbes-Med Tech Inc (Vancouver, Canada).

the mid-1960s. Also, high-oleic (*cis* 18:1) sunflower seed lines were produced in Russia in 1976 by selective breeding and mutagenesis (64), and were introduced and further developed in the United States in 1983 (64,65). High-oleic sunflower oil has better oxidative stability in deep-frying applications and extended shelf life compared to traditional sunflower oil. The latter has a higher content of linoleic (*cis* 18:2) than oleic acid and requires hydrogenation to enhance its resistance to oxidation. The high-oleic sunflower oil was commercialized in the United States in the late 1980s. However, holders of the patent on the high-oleic sunflower hybrid planting seed ($\geq 80\%$ oleic acid) were not willing to license the breeding materials to other companies, thus limiting the supply of high oleic sunflower oil and increased its cost relative to other commercial oils (66). The patent holder was, however, willing to license its mid-oleic breeding stock, which allowed the National Sunflower Association (Bismarck, ND) to develop the mid-oleic oil NuSun, released in 1998 (67,68).

Genetic molecular biology tools offer a more direct way

to modify fatty acid profiles (68-70). The resulting oil seed mutants are able to produce oils with a targeted fatty acid composition (see Table 2). For example, by chemical mutagenesis and genetic hybridization, soybean oil with a lower content of the more oxygen-labile linolenic acid (*cis*-18:3), and higher amounts of oleic acid (*cis*-18:1) was produced (71-74). This low linolenic/high oleic soybean oil has increased stability to oxidation, demonstrated by its longer shelf life and better performance in deep-frying applications. Other examples include canola oil seed mutants with low linolenic/high oleic acid content (75); soybean mutants with increased SFA, such as stearic (18:0) and/or palmitic acid (16:0), to augment solid fat content and hence avoid the need for hydrogenation (74); and soybean mutants with decreased SFA levels to enhance the nutritional/health value (74).

Many of these modified oils are now available on the market. Cargill Inc (Minneapolis, MN), under the brand names Clear Valley and Odyssey, offers mid- to high-oleic canola oils (65% to 85% oleic) with low content of linolenic acid (<3%) (ie, Clear Valley 65, 75, and 85, and Odyssey

Table 2. Fatty acid composition of various edible oil seeds and genetic variants

Variety	Fatty Acid Composition (g/100 g)					Origin	Reference
	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)		
Sunflower							
Traditional	7	4-6	20-30	60-70	<1	PB ^a PB	66
High oleic	5	4-5	80-90	5-9	<1		66
Mid oleic	4-5	4-5	55-75	15-35	<1		66
Soybean							
Traditional	11	4	23	54	8	PB/MTG ^b /GE ^c PB/MTG PB/MTG GE PB/MTG	74
Low linolenic	10-15	5-6	32-41	41-45	2		71-74
High palmitic	25	4	16	44	10		71
High stearic	9	26	18	39	8		71
High oleic	8	3	84	3	1		68
Low palmitic	4	3	25	58	8		68
Canola							
Traditional	4	2	62	22	10	GE	75
High oleic/Low linolenic	4	2	89	2	3		68
^a PB = plant breeding. ^b MTG = mutagenesis. ^c GE = genetic engineering.							

90 Plus 200) and high-oleic sunflower oils (80% oleic) with <0.5% linolenic acid (Clear Valley High Oleic Sunflower and Odyssey 100) (76). These oils have a high stability because of the low content of linolenic acid and are designed for deep-frying applications or for blending with other more saturated fats (see Table 1).

The National Sunflower Association marketed NuSun, a mid-level (65%) oleic sunflower oil (77). The NuSun sunflower germplasm lines were developed at the USDA Agricultural Research Service in Fargo, ND, by traditional plant breeding methods (78). Various other sunflower seed mutants have been engineered with mid-oleic acid levels (65% to 75% oleic acid) as well as hybrids that produce low levels of palmitic and stearic acids (66-70,79,80). Sunflower oil is naturally rich in tocopherols (vitamin E), which protect against oxidation/rancidity, and this trait has been perpetuated in the mutant germplasm lines. NuSun is recommended for deep-frying purposes, as it is resistant to oxidation over extended use, and it is currently being used in the new zero-*trans* Frito-Lay (Plano, TX) snacks (81) and zero *trans*-fat Crisco shortening (82).

Other edible oil companies have invested in the production of genetically modified oilseeds; some examples of them are displayed in Table 1 (83-86).

Tropical Oils

Palm, palm kernel oil, and coconut oils, having a high content of SFA (50%) and higher melting points, have been considered as candidates to replace partially hydrogenated solid fats, especially in bakery and confectionery goods. Fractionation of these oils by physical methods allows the isolation of fractions with different melting points suitable for numerous applications (87). For example, typical palm oil fractionation products are palm olein (soft fat), used as an ingredient in cooking and salad oils; and palm stearin (hard fat), used as an ingredient of

frying fats, shortenings, and margarines. Loders Crock-laan (Channahon, IL) has introduced in the market SansTrans, zero *trans*-fats prepared from palm oil. SansTrans features a range of palm oil fractions with different degrees of plasticity, varied content of saturated fatty acids (73% to 45%) and melting points (54°C to 16°C) that are suitable for bakery, confectionery, and deep-frying applications (88). Other products with similar characteristics as SansTrans are now available to the food industry. Some examples of these products are described in Table 1 (89-91).

Interesterification

Interesterification of mixed species of triglycerides is another option for the oil industry to produce customized fats with a range of melting points to suit different food-service applications. Interesterification is the hydrolysis of the ester bond between the fatty acid and glycerol and subsequent reformation of the ester bond among the mixed free fatty acids and glycerol. The resulting mixture of triacylglycerols contains fatty acid distributions representative of the starting fats. Interesterification can be achieved chemically or enzymatically. Chemical interesterification is a random process, but to a certain extent, the composition of fatty acids in the resulting interesterified triglyceride can be controlled by the relative amounts of each type of fat. During chemical interesterification there is substantial oil loss (approximately 30%) due to the formation of soap and fatty acid methyl esters (92). Enzymatic interesterification by the use of microbial lipases is more selective since lipases interact with specific triglyceride ester bonds (eg, 1,3-lipases). Enzymatic interesterification is preferred over chemical interesterification when a precise triglyceride composition is required (92,93). The major drawbacks of enzymatic interesterification are long reaction times (hours to days),

higher sensitivity to reaction conditions (eg, pH and temperature), and high cost (92,93).

Interesterification is usually done by blending high-saturated hard fats (eg, palm oil, palm stearin, and fully hydrogenated vegetable oils) with liquid edible oils to produce fats with intermediate characteristics. Chemical and enzymatic interesterification has been specially used in the formulation of margarines and shortenings (94,95) to provide products with no TFA but that still maintain physical properties, taste, and stability. Some of the zero *trans* margarines may have a higher content of saturated fatty acids (32% SFA, 0% *trans* fat) compared to conventional margarines that contain 8.5% to 23.4% SFA and 15% to 28% *trans* fat (43,95).

For example, ADM's (Decatur, IL) NovaLipid low-*trans*-fat line includes shortenings based on enzymatic interesterification of soybean and fully hydrogenated soybean and cottonseed oils containing 4% to 9% TFA (91).

Danisco (Copenhagen, Denmark), offers Benefat SALATRIM, which stands for short and long-chain triglyceride molecules (96). Benefat SALATRIM is produced by the interesterification of fully hydrogenated vegetable oils (containing C16 to C22 long-chain fatty acids) such as canola and soybean oil, with triacylglycerols of acetic, propionic, and/or butyric acids (short chain) (97). The resulting mixture of triacylglycerols contains short- and long-chain fatty acids randomly distributed on the glycerol backbone, with stearic acid as the predominant long-chain fatty acid (58 to 67 g per 100 g triacylglycerol) (98). Benefat SALATRIM is a reduced-energy fat due to the lower energy value of short-chain fatty acids and the incomplete absorption of stearic acid in the gastrointestinal tract, and provides approximately 5 kcal/g (98). Although Benefat SALATRIM was originally designed in the mid-1990s as a reduced-energy fat ingredient, its functional properties and fully saturated fatty acid pattern make it an attractive option for some food manufacturers to replace partially hydrogenated oil and reduce overall TFA in their products.

Kao Corporation (Tokyo, Japan) in partnership with ADM is marketing Enova in the United States. Enova is an edible oil composed principally of diacylglycerides (99). Enova is manufactured by 1,3-lipase-mediated-interesterification of unsaturated fatty acids derived from natural soybean and canola oils with glycerol. The content of diacylglycerides in Enova oil is close to 80% (see Table 1). Enova oil is part of a new generation of functional oils specifically designed to concurrently deliver nutritional and health benefits. Because diacylglycerides are not stored as fat in the body, it has been reported that consumption of oils such as Enova may have a positive effect in weight reduction and on blood lipid profiles (100).

Stepan Company (Northfield, IL) features a line of medium-chain triglycerides, with the brand name, Neobee. Neobee is based on caprylic and caproic acid triglycerides (101). Medium-chain triglycerides have a carbon chain length ranging from six to 10. Medium-chain triglycerides are not stored as fat, but are metabolized immediately by the body, and are reported to deliver similar nutritional and health benefits as products like Enova (102). One of the newer products that Stepan Company is offering is Neobee MLT-B, which is made from fully hydrogenated soybean oil, tristearin, and medium-chain

triglycerides (personal communication, Richard Tenore, Stepan Company, September 22, 2004) (see Table 1).

Med-Tech Inc (Vancouver, BC, Canada) has recently marketed Vivola oil, another edible oil that can be classified as a functional/nutraceutical oil (103). Vivola oil is composed of medium-chain triglycerides (65%), and fortified with n-3 and n-6 fatty acids and phytosterols. Vivola oil has been claimed to reduce body weight and to help lower LDL cholesterol (103).

Other Technologies/Products

Cargill Inc offers a line of all-purpose shortenings, TransEnd, which are made from a blend of high-oleic canola oil and fully hydrogenated soybean oil (76), with less than 2.0% TFA (see Table 1). The procedure employed to manufacture the TransEnd products is proprietary. Aarhus United (Port Newark, NJ) offers a nonhydrogenated shortening blend by the trademark name of Essence (90). The nature of the fats and procedure used in this shortening is proprietary; however, the product is described as TFA-free, containing 20% to 33% SFA, and compatible for blending with other edible oils.

TFA ALTERNATIVES IN RETAIL FOOD PRODUCTS

In 2002, a major snack food manufacturer, Frito-Lay (Plano, TX), announced that it was eliminating TFA in many of its salty snack products (104,105). Frito-Lay snacks (eg, corn chips and cheese puffs) are fried in low-linolenic mixtures of corn, soybean, and sunflower oil (NuSun brand) (81) instead of partially hydrogenated oil. Frito-Lay was among the first companies to declare the TFA content of their products in the Nutrition Facts panel (105). Also, Smuckers (Orrville, OH) recently introduced a 0 g *trans*-fat Crisco shortening. This shortening contains a blend of fully hydrogenated cottonseed oil, sunflower oil (NuSun brand), and soybean oil (82). The spreads Promise and Promise Light contain zero TFA and are formulated by interesterification of liquid vegetable oils with palm and palm kernel stearins (106). Some other examples of products that have been reformulated to reduce TFA are displayed in Table 3 (107,108).

POTENTIAL IMPLICATIONS OF TFA REPLACEMENT ON FATTY ACID INTAKE

As TFA are replaced by alternate fats, the potential exists for a significant change in the overall pattern of fatty acid consumption in the United States. The health implications of these changes deserve careful attention. For example, many of the TFA alternatives (Table 1) contain SFA, particularly tropical fats (eg, coconut, palm, and palm kernel oils), which for some time were avoided in US products due to their high SFA content (109). However, several controlled feeding studies have shown that palm oil, that contains 50% SFA (45% palmitic [16:0], 5% stearic [18:0]), 40% monounsaturated, and 10% polyunsaturated fatty acids has no detrimental effects on blood lipid profiles (109,110). In fact, in some studies, a slight positive effect on HDL cholesterol and lipoprotein a was noted (109,110). Experiments with animal models have indicated that palm oil shows antithrombotic effects similar to those exerted by polyunsaturated fatty acids (109).

Table 3. Examples of retail products with reduced <i>trans</i> -fatty acid (TFA) content			
Product	Manufacturer	Fat ingredients to reduce TFA	Reference
Frito Lay snack chips	Frito-Lay (Plano, TX)	High stability vegetable oils (eg NuSun)	81,104,105
Zero gram <i>trans</i> -fat Crisco shortening	Smuckers (Orville, OH)	Blend of fully hydrogenated cottonseed oil, high stability sunflower oil (NuSun), and soybean oil	82
Promise Light and Promise margarines	Lipton (Englewood Cliffs, NJ)	Interesterification of liquid vegetable oils with palm and palm kernel stearines	106
Land O'Lakes spreadable butter and soft baking butter	Land O'Lakes (St Paul, MN)	Blend of canola oil and cream	107
Goldfish crackers	Pepperidge Farm (Norwalk, CT)	Nonhydrogenated canola and sunflower (NuSun) oils	82
Fleischmann's margarine with olive oil	Fleischmann's (Omaha, NE)	Blend of olive oil, soybean oil, and fully hydrogenated soybean oil	106
New, Improved Reduced-Fat Oreo, Golden Oreo Original, and Golden Uh Oh! cookies; Honey Maid Low-Fat Cinnamon Grahams, Newton Fat-Free Fig Chewy Cookies; Triscuit Whole Wheat Baked Crackers; SnackWell Fat-Free Devils Food Cookie Cakes; SnackWell Cracked Pepper crackers	Kraft (Glenview, IL)	NA ^a	107
Zero <i>trans</i> -fat UTZ snacks	UTZ (Hanover, PA)	NA	108

^aNA=not available.

Unprocessed and processed palm oil contains rich amounts of tocopherols and tocotrienols (vitamin E), and crude palm oil is the richest natural plant source of carotene in terms of retinol equivalents (vitamin A) (110).

Individual SFA have been suggested to affect blood lipid profiles differently: lauric (12:0), myristic (14:0), and palmitic (16:0) acids increase LDL cholesterol levels, whereas stearic acid (18:0) has a neutral effect, attributed in part to its poor absorption (111,112). Lauric acid has been shown to decrease the total/HDL cholesterol ratio, due to a larger increase in HDL cholesterol (2,22). Mensink, Katan, and colleagues (2,22) have commented that even though consumption of SFA should not be promoted, lauric acid-rich palm kernel oil and coconut oil (approximately 50% lauric acid), in terms of effect on total/HDL cholesterol ratio, are still a better alternative for the food industry than partially hydrogenated oil in products that require solid fats for texture. Moreover, coconut and palm kernel oil are the basic sources of MCT (8:0 to 10:0) that are used in various low-energy and health products (see Table 1) (113).

Because TFA do not provide any known nutritional benefits and produce apparent unfavorable health effects, moving from TFA use to SFA use may produce a relative improvement in the dietary quality of processed foods that traditionally contained TFA. Nonetheless, the potential consequences of increased SFA in place of TFA in many processed products is a trend that deserves careful attention.

Alternative fats containing enhanced-oleic acid content to increase stability to oxidation, either through plant breeding or genetic modification, may possibly have negative health effects by reducing intake of the essential

fatty acids linoleic acid (n-6) and linolenic acid (n-3) and reducing the overall consumption of *cis*-polyunsaturated fatty acids (69). Linoleic and linolenic acid appear to be strongly protective against CHD, and to reduce LDL cholesterol level and the total/HDL cholesterol ratio (4,114). Currently, genetically modified vegetable oils are mainly used in industrial food frying applications, to replace partially hydrogenated oil (70).

CONCLUSIONS

Trends indicate that the edible oil industry will continue evolving to offer TFA alternatives to the food industry and in turn to the public. With the passing of the January 1, 2006 deadline for including TFA content on food labels, more products will appear on supermarket aisles bearing the label zero TFA or TFA-free. Also, because epidemiologic and clinical research indicate the importance of overall fatty acid intake, including the relative levels of n-3 and n-6 fatty acids and not simply reduction of *trans* and saturated fats, it is certain that functional fat alternatives with targeted fatty acid profiles will continue to evolve. The effect of this potential trend on overall fatty acid intake and consequent health implications deserves attention.

In addition, it is important to recognize that the changing fatty acid composition of processed foods will have a significant influence on the assessment of fatty acid intake by the US population. Updated and accurate TFA composition data for existing food products continue to be especially important to the evaluation of health status relative to dietary fat intake. Satchithanandam and colleagues (43) summarized the TFA composition of US

foods before the mandatory TFA labeling rule. Given the increased use of TFA alternatives, there is a clear need for ongoing sampling and analysis of foods to generate accurate, comprehensive, and publicly available food composition databases that can be used to track dietary intake of TFA and other fatty acids, and to study associations between the expected reductions in TFA intake and health risk factors. Selected foods are being analyzed for TFA content as part of the ongoing National Food and Nutrient Analysis Program (115), and the data are entered into the USDA National Nutrient Database for Standard Reference (42). However, the relatively frequent and continuing introduction of TFA alternatives to existing product formulations means that average database values may not accurately reflect the TFA content of individual samples of a particular food product, and in fact older and newer versions of a particular product/brand may coexist in the marketplace for some period of time. Therefore, researchers studying TFA intake and/or designing diets with targeted fatty acid composition should be particularly aware that snack foods, bakery items, confectionery items, and other products that have traditionally been made with partially hydrogenated oil may retain the same brand names yet have a significantly modified fatty acid content, and close attention to ingredient listings, nutrient composition data, and optional label claims on the exact foods used in research studies or in dietary recommendations is imperative.

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Mention of trade names, commercial products, or companies in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement of these products, over others not mentioned, by the authors, the USDA, or Virginia Polytechnic Institute and State University.

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Formulación de Productos Bajos en Grasas Trans

Nurhan Dunford
FAPC Oil/Oilseed Chemist

Ante la puesta en vigor de la nueva reglamentación en EUA respecto a la declaración en la etiqueta del contenido de grasas trans en los productos alimenticios, es importante conocer cómo se producen éstas y que alternativas tecnológicas existen para la formulación de productos con bajo contenido de grasas trans.



Las grasas y aceites comestibles consisten principalmente en triglicéridos, que son compuestos con tres ácidos grasos esterificados en la columna del glicerol. Las grasas y aceites de origen animal, como la mantequilla y la manteca de cerdo, están compuestos principalmente por ácidos grasos saturados. Los aceites y grasas derivados de las plantas contienen en su mayoría ácidos grasos mono y poliinsaturados, que incluyen respectivamente, uno o más dobles enlaces en su estructura química. En presencia del oxígeno, los ácidos grasos monoinsaturados y poliinsaturados se pueden deteriorar y enranciarse. Los fabricantes pueden reducir el deterioro y mejorar la textura del alimento al hidrogenar parcialmente la grasa insaturada.

La mayoría de los ácidos grasos insaturados naturales tienen estructuras

cis en sus dobles enlaces. La hidrogenación elimina algunos dobles enlaces y rearrregla otros, convirtiéndolos en configuración *trans*. La extensión de la hidrogenación determina cuanto aumenta el punto de fusión de la grasa resultante. Es por esto que los aceites vegetales (líquidos) se pueden convertir en productos que van desde margarinas suaves hasta grasas sólidas.

La calidad de los aceites comestibles se define por su estabilidad oxidativa, funcionalidad, y valor nutricional. Varias modificaciones técnicas de las grasas: hidrogenación, interesterificación, fraccionamiento, y combinaciones entre ellas se usan para mejorar la funcionalidad y estabilidad de los aceites. El cultivo de plantas y la biotecnología también se han utilizado ampliamente para desarrollar semillas con propiedades agronómicas requeridas y funcionalidad del aceite. Durante las décadas pasadas, se han in-

troducido algunas semillas con modificaciones en la composición de sus ácidos grasos. Algunas de estas semillas son la canola y la soya con bajo contenido de ácido linolénico; maíz, soya y girasol, así como cacahuate con alto contenido de ácido oleico; soya con alto y bajo contenido de ácidos grasos saturados. Muchos de estos aceites tienen un potencial importante para la reducción de grasas *trans*. Algunos estudios de laboratorio sobre freído con aceites altos en oleico y bajos en linolénico demostraron superioridad de los aceites modificados sobre los tradicionales. A pesar de que la mayoría de estos aceites modificados están hoy en día disponibles comercialmente, los costos y problemas de producción dificultan su uso como *commodity* en productos alimenticios.

El aceite de palma se puede separar en fracciones de oleína y estearina, las que posteriormente se pueden frac-

cionar en productos más duros o suaves. Algunos fabricantes reemplazan aceites hidrogenados en sus productos con estearina de aceite de palma (fracción de la grasa saturada). Ambos tipos de grasas, grasas *trans* y grasas saturadas, aumentan las lipoproteínas de baja densidad, las cuales contribuyen a la arterioesclerosis y al colesterol alto. Por lo tanto, los productos reformulados sin grasas *trans* no son más saludables que los alimentos que contienen los isómeros *trans*.

El aceite de palma se cristaliza más lentamente que otras grasas y aceites. Esto genera un fenómeno conocido como post-endurecimiento, en el que el producto se vuelve más duro durante su almacenamiento.

Las margarinas sin grasas *trans* que se preparan con aceites de semillas de girasol o algodón interesterificados con aceite de palma, aceite de nuez

de palma, estearina de palma y oleína de nuez de palma minimizan el post-endurecimiento. Existen estudios que indican que la preparación de leche descremada con emulsificantes antes a la cristalización retarda el endurecimiento posterior en mezclas que tengan alto contenido de aceite de palma o aceite de nuez de palma. Una interesterificación al azar de soya, maíz, cacahuete, semilla de algodón, canola y palma con soya completamente hidrogenada también produce productos que son adecuados para formular margarinas y mantecas con cero-*trans*.

Las mantecas líquidas son suspensiones estables de 2 al 20% de grasa sólida en aceites vegetales líquidos los cuales pueden o no estar hidrogenados. Estos productos se han estado utilizando en productos de panificación en donde no se requiere un alto contenido de sólidos, como en rellenos, pasteles y panes. Las mantecas fluidas mejoran la

suavidad y capacidad lubricante y sirve como portadores de emulsificantes necesarios para airear la pasta para pastel o dar fuerza a la miga del pan. Otras ventajas de las mantecas líquidas es que se pueden bombear e introducir fácilmente al proceso. Se puede lograr una cierta reducción en las grasas *trans* sustituyendo mantecas líquidas en formulaciones de alimentos.

El énfasis actual en la reducción de grasas *trans* en alimentos sin comprometer su calidad y sabor ha acelerado el desarrollo de nuevos ingredientes que se puedan usar como sustitutos de grasas *trans* en una variedad de aplicaciones, como pasteles, panes, alimentos fritos, sopas y salsas. Sans Trans Ultra (Loders Croklaan, Channahon, IL) es un sistema de emulsificación a base de aceite de palma con bajo contenido de grasas saturadas y pueden utilizarse en productos de panificación. Este producto no está hidrogenado, por lo tanto no contiene



Soluciones a la Medida para el Proceso de Alimentos

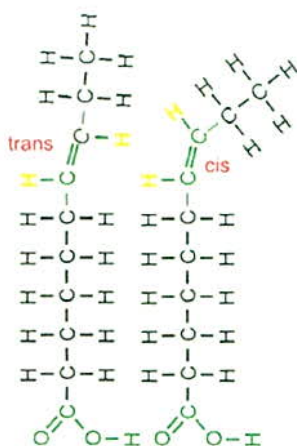
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grasas *trans*. De acuerdo con el proveedor, el sistema contiene grasas sólidas que se cristalizan fácilmente, ayudan a la aireación, y crema fácilmente con azúcar. Su punto de fusión y perfil lo hacen conveniente para pasteles, muffins, y rellenos para pastelería. La misma compañía también comercializa Durkex® NT 100, el cual es un aceite líquido no hidrogenado con alta estabilidad y bajo perfil sólido. Este producto se puede usar como portador de sabor, agente anti-polvos para sazónadores, especias, mezclas de bebidas, o cualquier polvo o cobertura para frutas secas y nueces.

En los Estados Unidos, los triacilglicéridos de cadena mediana, o MCT, son aceites que se han utilizado tradicionalmente en formulaciones dietéticas especiales y suplementos. Los MCT no son completamente metabolizados, por tanto proporcionan menos calorías. Estos aceites no son hidrogenados, por lo tanto son productos sin grasas *trans*. Han habido reportes que indican que los productos a base de MCT Neobee® MLT-B (Stepan Co., Maywood, NJ) se pueden utilizar como sustituto de aceites vegetales parcialmente hidrogenados en panificación.

TransEND® (Cargill, Minneapolis, MN) es una manteca a base de canola sin grasas *trans* altamente estable que se afirma iguala en funcionalidad, sensación bucal y estabilidad en vida de anaquel a las mantecas utilizadas convencionalmente, mantecas para pastel y coberturas, mantecas en palomitas para microondas, mantecas para engrasar. NovaLipid™ (Archer Daniels Midland Co., Decatur, IL) es una línea de aceites y mantecas bajos o sin grasas *trans* diseñados para utilizarse en panificación, para freír, confitería, botanas, cereales o margarinas. De acuerdo a la compañía, estos productos incluyen aceites naturalmente estables, mezclas de aceites y aceites interesterificados con enzimas que se pueden incorporar en alimentos sin comprometer la funcionalidad y nutrición. Vream Right y Vreamay Right son dos mantecas con grasas *trans* reducidas que fueron desarrolladas por Bunge Foods (Bunge Foods, Bradley, IL). Estos productos se han evaluado en varias aplicaciones. Según los reportes, se observaron pequeñas diferencias en galletas con chispas de chocolate y con azúcar, pasta de pies, y bisquets comparados con la formulación original. Los mismos productos bajos en grasas *trans* funcionaron similarmente al pastel control en blanco, amarillo, de chocolate y coberturas de crema.

Como se mencionó en un reporte anterior (FAPC-133 Trans Fats, Health and Nutrition Labeling of Foods), Unilever Canadá reformuló Imperial™, I Can't Believe It's Not Butter!™ Blue

Bonnet™, Golden Girl™, y Eversweet™ en productos sin grasas *trans*.

La margarina Becel no ha tenido grasas *trans* desde su lanzamiento en 1978. La margarina Canola Harvest Premium, margarina Fleischman's Light y la mantequilla light Smart Balance también son productos libres de grasas *trans* desde que la FDA anunció de las nuevas normas de etiquetado de grasas *trans*.

Pasos que se deben seguir antes de reformular productos Reducidos o sin Grasas Trans

Se recomienda que fabricantes de alimentos consideren los siguientes pasos antes de comenzar a reformular sus productos como productos reducidos y/o sin grasas *trans*:

- 1) Hable con proveedores de grasas/aceites sobre los tipos de ingredientes alternativos que ofrecen y cuanto cuestan.
- 2) Determine que tan confiable es el suministro de la grasa/aceite elegido y en que rango de precio fluctúa. Algunos proveedores no han escalado el proceso para la producción de aceites libres de grasas *trans* de la planta piloto al nivel de producción. Si la demanda de alimentos libres de grasas *trans* aumenta, podría haber un déficit en el suministro.
- 3) Compare procesos e ingredientes probando el producto en el laboratorio o en planta piloto. Recuerde que los perfiles de sabores y texturas específicas y su viabilidad para obtener los mismos resultados con el nuevo aceite son la clave para el éxito de su negocio.

Fuente:

Food and Agricultural Products Research and Technology Center
Oklahoma State University, FAPC- 134. 2004.

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IN THIS ISSUE: INCREDIBLE ENZYMES | HISPANIC MARKETING TRENDS

Generation NEXT

High-oleic oils promise stability gains and improved nutrition for baked foods and snacks. Blends get better, too.

BY LAURIE GORTON

Although not yet commercialized, a new generation of soybean oils — this time with high-oleic content — is poised to make yet another change in fatty acid profiles and functionality in baked foods and snacks. But plenty of progress also is occurring with shortenings and frying oils that have immediate market availability.

It's hard to imagine a basic category of bakery ingredients that has changed more than fats and oils. The big move out of animal fats into vegetable oils during the 1970s was only the tip of the iceberg. Today, choices on the plant-source oil menu encompass liquid and plastic shortenings far better suited to the healthy eating trend than any products before them. Whether produced by blending or breeding, the new oils eliminate trans fat, reduce saturated fats and bring omega-3 fats into everyday products. High-oleic oils are set to further improve stability and shelf life, a path blazed by low-linolenic styles a few years ago.

"There's been a lot of activity in oils, especially with formulations using high-oleic/low-linolenic canola oil and high-oleic/low-linolenic soybean oil" said Tom Tiffany, manager, oils and fats, R&D food applications, ADM Oils & Fats, Decatur, IL. "It's very exciting, as are the challenges to make improvements to blends to lower saturated fats without sacrificing functional benefits."

Nutritionally better fats and oils holds great promise. "It opens the baking industry's products to a whole new market of informed consumers willing to spend extra on healthier products," said Ernesto Hernandez, PhD, director of process development, OmegaPure, Houston, TX.

APPROVAL PIPELINE. Two new soybean varieties have almost finished the regulatory approval process required of genetically modified (GM) crops. The US

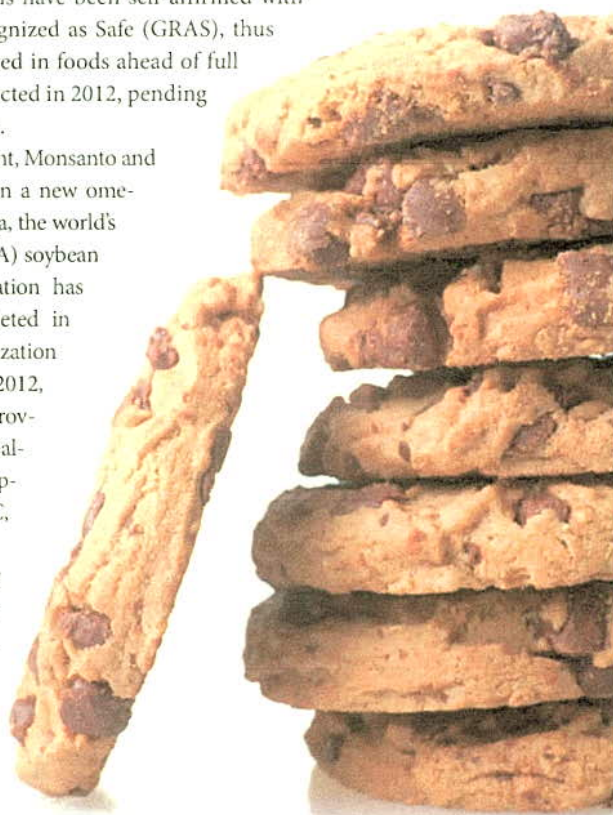
Department of Agriculture (USDA) granted approval in June 2010 to Plenish high-oleic soybeans, a project of Pioneer Hi-Bred, Johnston, IA. Its review by the Food and Drug Administration (FDA) was done in 2009. Vistive Gold, a low-saturate, high-oleic soybean developed by Monsanto Co., St. Louis, MO, completed its FDA biotechnology consultation in January 2010, and its USDA petition is currently under review. The oils extracted from these new soybeans have been self-affirmed with FDA as Generally Recognized as Safe (GRAS), thus allowing them to be tested in foods ahead of full commercialization, expected in 2012, pending full regulatory approvals.

In a related development, Monsanto and Solae are collaborating on a new omega-3 oil for food: Soymega, the world's first stearidonic acid (SDA) soybean oil. FDA GRAS notification has been successfully completed in 2009, and commercialization is anticipated around 2012, pending regulatory approvals, according to Al Gallegos, business development director, Solae, LLC, St. Louis, MO.

"The food industry needs fats and oils with positive flavor and

► Omega-9 oils, created by plant breeding, help cut partially hydrogenated shortenings — and trans fats — out of cookies.

DOW AGROSCIENCES



mouthfeel, extended shelf life, healthful nutritional profile, surety of supply, easily discovered price structure, affordable price and multiple suppliers," said Richard Galloway, president, Galloway & Associates, Isle of Pines, SC, a consultant for Qualisoy, St. Louis, MO.

Plenish and Vistive Gold are trait-enhanced soybeans, supported in their development by Qualisoy, a collaborative project of the soybean industry formed by the United Soybean Board, St. Louis, MO.

"Why put such traits into soybeans?" asked Susan Knowlton, PhD, research scientist, Pioneer Hi-Bred, a DuPont business, Wilmington, DE. "It's because soy is grown on more acres than any other US oilseed crop.

sunflower, but other oils with less desirable properties," he observed.

Plenish has agricultural approvals from regulatory agencies in North America as well as Australia and New Zealand, among others. "We anticipate commercialization in 2012," Dr. Knowlton said.

Monsanto noted that approval of Vistive Gold in North America is expected within the next year or two, pending full approvals. "Things are happening," said Rick Wilkes, food applications director, Monsanto Co.

Testing in foods is what's happening now. "Testing can be a long process," Dr. Knowlton observed. "People should be thinking applications today because of the long lead times involved, not only on supply but also to understand the oil's properties." This is true for bakeries and food manufacturers as well as food service users, who need to qualify the fry oils in their operations.

Bakers face a very real challenge, according to Don Banks, president, Edible Oil Technology, Dallas, TX, a consultant to Qualisoy. "To make various items, bakers have long used one or two multipurpose shortenings, the so-called all-purpose shortenings, made with partially hydrogenated oils," he explained. "Now, they want trans-free products that directly replace the partially hydrogenated shortenings, and they want the cost, functionality, performance and so forth to remain the same." The trait-enhanced soy oils developed through Qualisoy efforts address the need for fats and oils with low-linolenic, low-saturate and high-oleic content.

IN THE MARKET. New oilseed varieties developed through conventional plant breeding techniques do not face the same regulatory hurdles as GM plants. Such non-GM vegetable oils are also making news.

The oils extracted from Nexera canola and sunflower hybrids, developed conventionally by Dow AgroSciences and grown under identity-preserved (IP) contracts with farmers in Canada and North Dakota, are high in unsaturated fats. The company branded the oil as Omega-9 to call attention to its high monounsaturated fat content, according to David Dzisiak, commercial leader, oils, Dow AgroSciences, Indianapolis, IN.

"We are an agricultural sciences company," Mr. Dzisiak explained. "When trans fat labeling hit in 2005, we evaluated alternatives. Through plant breeding, you can change the fatty acid profile and create naturally stable oils that don't need hydrogenation." His colleague, Dave Booher, group leader, healthy oils, observed that canola is North America's second most widely used food oil.

The newest addition to Cargill's Clear Valley line is a low-saturate canola oil. "Through plant breeding, we brought canola from 7% saturates to 4% saturates," said Lorin Debonte, PhD, assistant vice-president, R&D, Cargill Specialty Canola Oils, Wayzata, MN. "We will be



▲ Among other uses, high-oleic soybean oil, a biotech product, can serve as a spray oil for crackers as well as a shortening base for cookie applications.

UNITED SOYBEAN BOARD

Not only is it a lower-cost oil, it also naturally contains antioxidants that lead to its stability. And it is a preferred flavor among US consumers."

Specifically, the trait enhancement raises the level of oleic fatty acids and lowers the linolenic content, thus increasing the oil's proportion of stable fatty acids and cutting the less stable ones. This change aims to eliminate the need for partial hydrogenation to protect oils against oxidation and, thus, formation of trans fats.

Current commercial options for cutting trans fats in shortenings are palm and high-oleic canola oils, according to Mr. Galloway. Sunflower oil is also used. "I don't see the new oils replacing canola and

able to use it as a liquid oil and to blend bakery shortenings." Samples are available for prototype work, and full commercialization is projected for 2014.

Described as the next generation in cooking oils, high-oleic non-GM canola oil marketed by SK Food International, Fargo, ND, allows longer fry times and extended shelf life, according to LeAnn Hovdenes in business development with SK Food. It is expeller-pressed, a process that does not use solvents or chemicals. • e company recently added US-origin, IP, non-GM corn oil.

"Customers are becoming increasingly aware of product origin and want more information about content and production methods," Ms. Hovdenes said. "• ey also want assurance that product identity and characteristics have been preserved for full traceability."

Nutrisun, a non-GM sun•ower oil with high stearic and oleic content debuted in mid-2010. Developed by Advanta, Mar del Plata, Argentina, in conjunction with CSIC Spain in Madrid, Spain, the new sun•ower variety grows in Texas, Kansas, Oklahoma and South and North Dakota. It is marketed in the US by Technology Crops International, Winston-Salem, NC. "• is innovative oil suits the needs for foods that require use of stable fats," said Alice Coram, a spokesperson for Technology Crops.

Reducing With Microdroplets

Much of the appeal of buttercream-style icings depends on the shortening used, which makes their smooth texture and spreading ability difficult to replicate in low-fat frostings. Microdroplets of trans-fat-free oils, encapsulated in cornstarch or wheat flour, may solve this problem, according to researchers at the USDA's Agricultural Research Service, Peoria, IL.

Led by Mukti Singh, PhD, a USDA-ARS food technologist in the Functional Foods Research Unit, researchers also made cakes using the Fantesk-branded ingredient without adding oil, creating a low-fat product with improved texture and volume. The icings contained 50% less fat.

Fantesk is a mixture of starch, water and one or more liquid oils, which is then processed in pressurized superheated steam to form an unusual gel. Regardless of subsequent processing — melting, freezing or drum-drying — the tiny oil droplets remained dispersed in the starch. Covered by patents, Fantesk has been licensed, and licensees are working to commercialize its production.

The development was described in the March 2010 issue of *Agricultural Research* magazine, published by USDA and available on the department's website, www.ars.usda.gov.



▲ Addition of DHA to shortenings and oils boosts the nutritional profile of foods while retaining traditional fat functionality.

MARTEK BIOSCIENCES

OPERATING BENEFITS. The next-generation oils are moving forward with applications. The first marketing program for Monsanto's Vistive Gold targets healthy frying. The FitFrying partnership addresses food service issues and brings together Bunge, Monsanto and Qualiso among its partners, as well as Frymaster, Lamb Weston, Alconox and the Idaho Potato Commission.

"We are thrilled to be part of this partnership that represents the entire value chain from seeds to fryer equipment," said Philippe Ballet, food business development director, Monsanto Co. "It all begins with the seed. We can put a lot of technology up front in order to provide a better fried food. Testing has demonstrated the oil to have excellent stability and flavor. Tested with french fries, saturated fat content was significantly reduced."

Vistive Gold oil contains 68 to 74% oleic acid, with saturates reduced from the 15% typical of commodity soy oil to 6%, and most of that is palmitic (75% reduction), according to Mr. Wilkes. • e result is an oil that can replace trans fats and provide benefits such as reduced saturated fat and as stability, particularly important in the production of french fries, potato chips and donuts. "Its stability • ghts fat's tendency to polymerize in the fryer and, thus, solves operational problems, too," he noted.

Stability against oxidation lengthens the life of fry oils and • nished foods. • e lower the linolenic content, the



▲ GRAS status enables food companies to test new high-oleic oils before commercialization, expected in 2012.
DUPONT / PIONEER HUBRED

more stable the oil. Partially hydrogenation increases resistance to oxidation, but greater natural stability of high-oleic oils eliminates that need.

"Plenish high-oleic soybean oils exhibit greater fry life, up to three times longer than commodity oils," Dr. Knowlton reported. "As for consumer benefits, it has 0 g of trans fats, 20% less saturated fat than commodity soy oils and 75% less saturated fat than palm. We're really excited about this oil and hope the industry will be, too."

Dr. Knowlton said that Plenish is being evaluated as a potential base oil for shortenings that could be blended with solid fats such as cottonseed or palm to achieve the desired plasticity. "With high-oleic oils, you can create shortenings with lower saturated fat levels than with palm alone and thereby provide a shortening product with longer shelf life in the end product, as well as the nutritional advantages of a low-sat shortening," she said. Additional uses include high-stability spray oils for crackers and pan-release oils.

OMEGA-3 CONTENT. Oils high in SDA address the nutritional need to increase consumption of omega-3 fatty acids. Although soybean oil contains alpha-linolenic



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For more information, see Page 121

acid (ALA), an omega-3, the lack of eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) — both polyunsaturated omega-3s — in contemporary human diets prompted the Monsanto-Solae Soymega project to develop soy oil with SDA. The body rapidly turns SDA, an intermediate between ALA and EPA, into EPA.

Soymega oil will find use in baked foods and snacks either as a direct ingredient in formulations or in the form of margarine or shortening. "SDA oils compare favorably with other omega-3 oils in taste and are easier to incorporate into foods than DHA and EPA," Mr. Gallegos said.

"Soymega is a great solution for food companies that want to add omega-3s to everyday foods, including bakery products, and provide consumers with more options to get omega-3s into their daily diet," observed Jane Whittinghill, senior research investigator, analytical science group, Solae, LLC.

Omega-3 content is the main feature of another new Clear Valley oil from Cargill. It blends high-oleic canola and flaxseed oils and is suitable for cookies, crackers and chips. "It can be used at rates to justify 'good' (160 mg per serving) and 'excellent' (320 mg per serving) claims for omega-3s," Dr. DeBonte said. "Consumer awareness of omega-3s allows food processors to sell more and charge more."

Pioneering DHA applications in foods, Martek Biosciences Corp., Columbia, MD, is seeking larger-scale applications for its life's DHA such as bakery. "We're currently working with Dow AgroSciences to develop a canola seed that produces DHA," said Christine Bunting, director, applications and technical service, Martek Biosciences.

Fish oils, the conventional source for omega-3s, are being improved, too. "Development of new antioxidants for our fish oil allowed us to efficiently blend it with baking fats

and be able to withstand oven temperatures to produce a wide variety of baked products," Dr. Hernandez said. OmegaPure fish oils can be added through blending with the other fats, put into the baked product premix, encapsulated or blended

with milled flaxseed or incorporated into pre-made inclusions.

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sources to meet the functional and fatty acid profile needs of bakers.

To effect nutritional improvements such as elimination of trans fats and hydrogenation, Loders Croklaan developed shortenings that also reduce saturated fats, total calories and calories from fat, with bakery applications in mind. "In addition to the nutritional benefits, all of the products provide excellent performance where a solid fat is required for functionality," said Gerald McNeill, PhD, vice-president, R&D and marketing, Loders Croklaan North America, IOI Group, Channahon, IL. "In most cases, there is no cost increase, and some of the products provide a significant cost reduction."

The company's SansTrans VLS 23 **shortening blends canola, palm and palm kernel oil**. Dr. McNeill explained that palm kernel oil contains only 23% saturated fat, compared with 50% in palm oil, and is semi-solid and functional in cookies and crackers. SansTrans VLS 30 and VLS 40 provide a 15% fat reduction without the need to extensively reformulate cookies, muffins and cakes. "Benefits include lower saturated fat, lower total fat and lower calories, as well as a cost saving of about 10% or more compared with standard all-purpose shortening," he said.

The new Satin Glo line of liquid shortenings from Mallet & Co., Carnegie, PA, provides another good example. "We designed these to replace partially hydrogenated plastic shortenings, as well as palm-based shortenings," said Bob Wilhelm, Mallet's vice-president of R&D. "They are lower in saturated fats than other trans-free choices yet are functionally equivalent to plastic shortenings and consistent in performance in bakery applications. They allow cleaner labels and give similar outcomes to the shortenings they replace."

Bunge employs enzymatic interesterification (EI) to modify soybean oils for its UltraBlends line of drop-in replacements for traditional shortenings and margarines. "Use them as you would a traditional margarine, shortening or fry product," said Roger Daniels, director, R&D, Bunge Oils, Bradley, IL. "Actually, these products get the baker back closer [to the performance of fats and shortenings] of 30 years ago."

Bill McCullough, director of marketing, Bunge Oils, explained, "The vision here is to reduce trans fats by using domestic soy oils."

The company puts balanced blends of liquid oil and hard stock through its patent-applied-for oil purification step and subsequent EI process in a way that ensures consistent product characteristics in melting profile and basic quality attributes. Mr. Daniels said that EI randomizes the fatty acids present at triacylglycerols in positions No. 1 and No. 3 on the fat molecules. This method creates a wider variety of melting triacylglycerides than previously present in the oil, thus giving the baker the

▲ Palm oil balances saturated and unsaturated fats. Leveraging of palm oil fractions brings shortening functionality to blended fats.



appropriate hardness or stiffness in the dough for the intended end-use application. The process also enhances the plasticity range of the shortenings.

Ventura Foods uses domestic oils to produce NTrans, a no-trans, lower-saturates product, and the result is a shortening that adds only two ingredients to the package label, according to Frank Stynes, senior vice-president, industrial group, Ventura Foods LLC, Brea, CA. "We have spent the vast majority of our time on no trans, reduced saturates and generally cleaner-labeled products for our customers," he said. "Because of the limitations of processing—in other words, no hydrogenation—these are not 'drop in' replacements. Some can be directly substituted, but some require customers to adjust their processes to use these products."

A pioneer in the trans-free market, AAK, Port Newark, NJ, blends liquid oils (canola, soy and other sources) with a proprietary hard stock derived from palm and palm kernel oils, which are natural sources of solid fats. The resulting EsSence brand shortenings are trans-free, nonhydrogenated and low in saturated fat.

The shortening range can be used in cookies, pie shells, biscuits, wafers and breakfast foods, and they are suitable as frying fats. The company developed a trans-free solution for laminated doughs and puff pastry, among the most demanding of baked foods applications.

As bakers begin to work with the emerging next-generation fats and oils, they can anticipate highly functional choices to replace the hydrogenated shortenings that have been so important to this category. Some will result from trait improvement through conventional plant breeding and biotechnology; others will come out of process innovations for modifying and blending today's oils. But all will foster plenty of creativity. ■



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Contenido En Acidos Grasos Trans de las Margarinas: Evolución en las Últimas Décadas y Tendencias Actuales.

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TÍTULO ABREVIADO: ÁCIDOS GRASOS TRANS EN MARGARINAS

Resumen

El proceso de hidrogenación llevado a cabo en la industria para obtener margarina conlleva la formación de una cierta cantidad de isómeros *trans*. El consumo de este alimento así como la cantidad de estos isómeros que contiene, han sido motivo de gran controversia en las últimas décadas. Mientras que en la década de los ochenta, se consideraba saludable el consumo de margarina, en la década de los noventa numerosos estudios indicaron que el 18:1t, incrementaba las concentraciones de LDL-colesterol y reducía los niveles de HDL-colesterol, además de asociar su ingestión con un incremento del riesgo de sufrir enfermedad coronaria. La creciente publicidad sobre los efectos desfavorables de los ácidos grasos *trans* parece haber influenciado a los productores de margarina, a reducir la cantidad de estos isómeros en sus productos. Mientras tanto, Estados Unidos ha adoptado una legislación para especificar su contenido en el etiquetado de los alimentos y en Europa, Dinamarca ha limitado los niveles máximos permitidos en los alimentos.

Palabras Clave: margarina, ácidos grasos trans, salud, etiqueta.

SUMMARY

Trans fatty acids isomers are formed during the hydrogenation process used in the food industry to harden oils. In the last decades there has been a great controversy about the consumption of margarine due to the levels of trans fatty acids they contain. While in the eighties consumption of margarine was considered healthy, during the nineties several studies indicated that consumption of 18:1t increased LDL-cholesterol levels and decreased HDL-cholesterol level, and was related with an increased risk of coronary heart disease. The publicity about the unfavourable effects of trans fatty acid consumption seems to have influenced margarine producers to reduce the trans fatty acid content of margarines. Meanwhile USA has adopted a new legislation about trans fatty acid labelling. In Europe, Dinamarca has limited the maximum level of trans fatty acids allowed in food products.

KEYWORDS: margarine, trans fatty acids, health, label.

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Margarines Trans-Fatty Acid Composition: Modifications During the Last Decades and New Trends.

Introducción

Las margarinas son alimentos para extender preparados con una mezcla de grasas y/o aceites con otros ingredientes tales como agua y/o producto lácteos, etc. (1). A menudo se fabrican combinando grasas sólidas y un aceite. Las primeras pueden prepararse con aceites hidrogenados y una mezcla de grasas sólidas naturales o grasas interesterificadas. El segundo suele ser aceite de girasol, canola, soja, y, ocasionalmente, aceite de oliva.

El proceso de hidrogenación se lleva a cabo en la industria para obtener grasas con características reológicas apropiadas. Este proceso conlleva a la formación de una cierta cantidad de isómeros respecto a los ácidos grasos de origen, en los cuales se modifica la configuración *cis* a *trans*. Este cambio tiene repercusión nutricional. Entre otros efectos, se produce una pérdida funcional de las propiedades de los ácidos grasos esenciales, e, más, compiten con estos e inhiben la actividad de la enzima Δ -6-desaturasa. Las implicaciones fisiológicas de esta inhibición en los niños son en gran parte desconocidas (2).

Otro efecto negativo que se le atribuyen a estos isómeros se produce sobre el metabolismo de las lipoproteínas. Diversos estudios indican que el 18:1t incrementa las concentraciones de LDL-colesterol, comparado con los ácidos oleico y linoleico (3)(4)(5)(6). Sin embargo, los efectos sobre la HDL son menos consistentes; así algunos estudios no detectan ningún efecto (7)(8)(9), mientras que de Roos et al. (10) indican que estos isómeros provocan un incremento en la relación colesterol LDL/colesterol HDL aproximadamente el doble al originado por las grasas saturadas. También pueden atribuirse a los ácidos grasos *trans* pequeños incrementos en los niveles de Lp(a) (9)(11).

Debido a estas evidencias, la Administración de Alimentos y Medicamentos de Estados Unidos (FDA) ha propuesto la inclusión de los ácidos grasos *trans* en el recuadro de la Declaración Nutricional para alimentos que contienen más de 0,5 gramos de grasa *trans* por ración (12). En el etiquetado nutricional, después del encabezado "Grasas saturadas", un símbolo como un asterisco informará a los consumidores de una nota al pie que señala que el producto "incluye x g de grasa *trans*". Si un alimento contiene menos de 0,5 gramos de grasa *trans*, dicha etiqueta será opcional, ya que los métodos analíticos no pueden medir niveles menores de una manera confiable. Este etiquetado debe estar presente en todos los productos alimenticios antes del 2006 (13). En este sentido, Dinamarca ha sido el primero en poner un límite legal al contenido de ácidos grasos *trans* de lo

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alimentos, mediante una legislación interna que impide la comercialización de productos que contengan más de un 2% de dichos ácidos grasos desde el 2004. El Danish Nutrition Council recomienda que antes de que acabe el año 2005 cese el uso de ácidos grasos trans en la elaboración de los alimentos, y hasta entonces la declaración de su contenido está siendo obligatoria (14).

El consumo de margarinas y su incidencia sobre la salud

Ha habido gran controversia acerca de la seguridad en el consumo de las margarinas. Así, en la década de los ochenta se aseguraba que las mismas podían consumirse con total seguridad por ser fuente de ácidos grasos poliinsaturados, carecer de colesterol y contener poca cantidad de ácido grasos saturados (15); otros autores (16) sostienen que eran fuente de vitamina E y esteroides tales como: sitosterol, campesterol y estigmasterol todos ellos con importancia significativa en la dieta.

Sin embargo, desde la década de los noventa, numerosos estudios mostraron que el 18:1t incrementaba las concentraciones de LDL-colesterol (17) (18)(19)(20)(21) y reducía los niveles de HDL-colesterol (18)(19)(21). Otros estudios epidemiológicos realizados (17)(18)(22)(23), proporcionaron evidencias de una relación positiva entre ingesta de ácidos grasos trans e incremento del riesgo de sufrir una Enfermedad Coronaria (EC). Sin embargo, científicos respaldados por el Instituto Americano de Nutrición, manifestaron que no se podía correlacionar la ingesta de estos ácidos grasos con dicha enfermedad (25). Es por ello que se sucedieron numerosas publicaciones para aclarar este asunto. Así, Tavani *et al.* (26) en un estudio llevado a cabo en 429 mujeres italianas de entre 18 y 74 años de edad, observaron que una ingesta elevada o media de margarinas se asociaba con un incremento en el riesgo de padecer infarto agudo de miocardio. En el mismo año Hu *et al.*, (27) publicaron una valoración epidemiológica con datos basados en 80.082 enfermeras americanas entre 34 y 59 años de edad donde llegaron a la conclusión de que era más efectivo para la prevención de enfermedades coronarias en mujeres, reemplazar las grasas saturadas y trans insaturadas por grasas no hidrogenadas monoinsaturadas o poliinsaturadas, que reducir la ingesta total de grasa. Cierra esta década y abre la siguiente el estudio TRANSFAII (28)(29) llevado a cabo en 14 países del oeste de Europa, en el que no se encontró correlación positiva entre ingesta de trans y riesgo de EC aunque se aconsejaba la disminución de la ingesta de ácidos grasos elevadores del colesterol, entre ellos los ácidos grasos trans. En el estudio de Ancianos de Zutphen (30) participaron 667 hombres holandeses con edades comprendidas entre 64 y 84 años, llegándose a la conclusión de que la ingesta de ácidos grasos trans estaba positivamente asociada al riesgo de EC.

Contenido en ácidos grasos trans de las margarinas en la década de los ochenta

En esta década se observa una gran variabilidad en el contenido de ácidos grasos trans en margarinas, que oscila desde su ausencia hasta niveles superiores al 30% (Tabla 1). En el estudio realizado por Enig *et al.* (31) en 40 muestras de margarinas de Estados Unidos se encontraron niveles similares a los registrados en la década anterior en margarinas de ese mismo país y de Canadá (32)(33).

Tabla 1. Niveles máximos y mínimos (% de ácidos grasos totales) de ácidos grasos trans en margarinas en la década de los ochenta.

C14:1t	C16:1t	C18:1t	C18:2t	C18:3t	Trans totales	País (Referencia)
-	-	5,70-21,7	0,60-6,60	-	7,3-22,4	USA (34)
-	-	6,80-31,0	Nd-5,2	-	-	USA (31)
-	-	10,7-30,1	0,21-4,78	-	-	USA (37)
-	-	0,10-32,7	0,05-1,48	-	0,30-34,70	España (36)
-	-	0,00-16,03 0,00-6,60 *	0,00-0,51 0,00-0,59 *	-	0,00-16,54 0,00-7,19 *	España (35)

* Margarina elaborada con grasas de origen vegetal y animal

Es de destacar la mejora de las técnicas analíticas, así la longitud de las columnas usadas en la cromatografía de gases varía de los 6,1 m de los trabajos de Glidenberg y Firestone (34) y de Coll y Gutierrez (35), de 15 m en el de Enig *et al.* (31), pasándose a la de 50 m en el trabajo de Hernández y Boatella (36), hasta la de 100 m en el de Slover *et al.* (37). Obviamente, se consiguieron mejores separaciones de los distintos isómeros de los ácidos grasos con la última columna, ya que en las primeras sólo podían darse los valores de los ácidos trans monoenoicos como C18:1t y los del trans dienoicos como C18:2t, que expresaban la suma de los distintos isómeros de cada uno de ellos, llegándose a identificar con la columna de 100 m individualmente a los isómeros del primero como: 13t; 12t + 10t; 9t + 11t + 13c; 8t; 7t, 6t; 7t y 12c + 11c + 5t; y a los de segundo como: 9t, 12c; 9c, 12t; y 9t, 12t. Cabe decir que con la columna de 50 m, aunque no se lograron separar los distintos isómeros de octadecenoicos, se separaron los tres del octadecadienoico mencionados anteriormente (36). Esto también había sido observado en un trabajo de Sampugna *et al.* (38) comparando columnas de 15 m y 75 m.

Se aprecia también en esta década que no se identifican los isómeros trans de los ácidos miristoleico, palmitoleico y linolenico, siendo lo mayoritarios los del oleico y linoleico, en ese orden. El origen de estos es atribuible a la hidrogenación parcial de los aceites nativos, que originan isómeros de posición y geométricos de dichos ácidos grasos. Dicha hidrogenación, que es probablemente la mayor herramienta de los productores de margarinas, tiene la finalidad de reducir el grado de insaturación y elevar el punto de fusión del aceite. El proceso normalmente no se hace completo, porque las grasas totalmente saturadas tienen puntos de fusión muy elevados y sin las características plásticas deseadas (39).

Finalmente destaca el menor contenido de ácidos grasos trans en las margarinas españolas (35) elaboradas en esta época mayoritariamente con una mezcla de grasas de origen vegetal y animal, ya que estas últimas contienen dichos isómeros en pequeña cantidad, procedentes de la alimentación del animal.

Contenido en ácidos grasos trans de las margarinas en la década de los noventa

Esta década se inicia con la afirmación de que la ingesta de ácidos grasos trans en condiciones normales no ejerce efectos adversos para la salud siempre que se ingieran cantidades adecuadas de ácidos grasos esenciales; se destacaba, sin embargo, la necesidad de buscar métodos analíticos fiables para la determinación exacta de la cantidad de estos ácidos grasos en los distintos alimentos. La publicación de los trabajos mencionados anteriormente sobre una asociación positiva entre consumo de trans y enfermedades cardiovasculares incrementó dicha búsqueda.

Para ello se extendió el uso de columnas capilares de 50 m y 60 m en la mayoría de los trabajos (Tabla 2), así como de 100 m (41, 42), siendo la excepción la de 4 m utilizada por Block y Barrera (43). Ratnayake y Beare-Rogers (40) realizan una separación previa en cromatografía en capa fina con nitrato de plata para mejorar la separación posterior de los distintos isómeros en el cromatógrafo gas-líquido, logrando identificar los siguientes isómeros del C18:1t: 6t-11t; 12t-13t; 14t y 15t; por su parte, los del C18:2t identificados fueron: 9t, 12t; 9t, 12c; ct/tc; 9c, 12t y 9t, 12c. En cuanto a los isómeros del C18:3 identificados fueron los siguientes: 9c, 12t, 15t + 9t, 12c, 15t; 9t, 12c, 15c y 9c, 12t, 15c. Los demás autores no separan los distintos isómeros del C18:1t, aunque en algunos casos separan varios de los isómeros del C18:2t (41, 42, 44). Por su parte, Fernández Sar Juan (45) identifica los ácidos elaidico y linolelaidico, aunque los denomina C18:1t y C18:2t, respectivamente.

Se aprecia, en las distintas investigaciones realizadas, la tendencia a no detectar C14:1t en las margarinas analizadas (Tabla 2), excepto por Fritch y Seinhart (44), que lo encuentran en pequeña cantidad. Por su parte, el C16:1t es detectado en aquellas margarinas que han sido elaboradas con aceites de pescado hidrogenados. En relación a dicho ácido graso puede destacarse que su contenido aumenta al incrementarse la dureza de la margarina (46)(47), lo que indicaría su formación en el proceso de hidrogenación a que es sometido el aceite de pescado en su endurecimiento por convertirlo en margarina. En relación al C18:3t, destacan las cantidades reducidas de los mismos. Según Ackman *et al.*, (48) la presencia de los isómeros trans geométricos de los ácidos linoleico y linolénico en las margarinas se debe a que las mismas están constituidas por aceites refinados y desodorizados por procedimientos físicos, ya que al exponer los aceites a elevadas temperaturas se forman dichos isómeros; sin embargo no siempre están presentes en los aceites refinados, indicando la gran variación existente en las prácticas de los procesos de refinación (31).

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Tabla 2. Niveles máximos y mínimos (% de ácidos grasos totales) de ácidos grasos *trans* en margarinas en la década de los noventa

C14:1t	C16:1t	C18:1t	C18:2t	C18:3t	Trans totales	País (Referencia)
-	-	12,50-34,2	0,60-6,90	0,30-0,60	14,39,1	Canadá (40)
-	-	3,50-17 0,00-4,2	0,00-0,40 0,00-0,01	-	0,00-17,8 0,00-4,20	España (45)
-	-	-	-	-	10,80	España (71)
-	0,00 † 0,00 † 0,95 ††	12,13 † 10,10 † 4,05 ††	0,00 † 0,59 † 0,40 ††	-	-	Finlandia (46)
-	-	0,10-23	0,1-1,7	-	0,6-23,5	Alemania (72)
-	-	-	-	-	13,4-38	Brasil (43)
-	-	0-20,10	0-0,70	-	0,40-21	Alemania (72)
-	-	-	-	-	16,80	España (74, 75)
-	-	0,2-22,3	0-1,0	0-1,4	0,5-24,5	Bélgica (49)
-	-	0,10-9,90	0,30-0,90	-	0,80-10,20	Malasia (76)
-	-	-	-	-	0-10,6	Alemania (77)
-	-	10,9-17	0-2,8	0-0,8	12,6-19,7	Nueva Zelanda (41)
-	-	0,04-13,29	0-0,26	-	-	USA (78)
< 0,01	0-0,03	0,05-4,4	0-0,43	-	0,15-4,9	Alemania (44)
-	-	Nd-15,35 Nd-2,00* 0,20-15†	-	-	0,12-16,5 0,10-2,60* 0,5 0-16,0†	Europa (14 países) (79)
-	Nd † 0,0-2,9 † 0,0-3,7 ††	0,00-1,9 † 0,00-5,8 † 0-14,2 ††	-	-	-	Dinamarca (47)
-	-	0,20-35 † 14,80-37,0 †	0,20-9,60 † 0,60-8,70 †	0,00-17,5 † 0,10-1,20 † †	18,80 † 34,30 †	Canadá (42)
-	-	1,90-8,00	0,40-1,40	-	-	Bulgaria (80)

* Margarina suave baja en *trans* † Margarina suave alta en *trans* ‡ Margarina suave
Margarina semiblanda †† Margarina dura ** Margarina elaborada con grasas de origen
vegetal y animal

El isómero mayoritario en las margarinas es el C18:1t (> 90 %) (49). Dentro de éste, el ácido eláidico (t-9) frecuentemente ha sido el isómero más importante en margarinas (50) aunque también se ha encontrado como mayoritarios junto a él, al t-10, con una media de 24% y 21% respectivamente, seguidos del t6-8, con 18,5 %; t12 y t13-14 con alrededor de 10%; t15 y t16 que representan aproximadamente el 1% del total de estos isómeros, y finalmente t4 y t5, que no alcanzan el último porcentaje citado (51).

Por su parte, Hyvönen *et al.*, (46) identifican isómeros *trans* del C20 y C22, aunque solo en las margarinas duras, las cuales se elaboran con aceite marinos hidrogenados.

Tendencias actuales

Se aprecia en la Tabla 3 que el contenido medio de ácidos grasos *trans* en muestras correspondientes al año 2000 y posteriores son inferiores a la detectadas en décadas anteriores. Así en las margarinas austriacas se detectan los niveles más bajos, del 1,60% (52), seguidas de las portuguesa (53) y españolas (54), ambas con 2,50%. Destaca además que dicho contenido asciende según lo hace la dureza de las margarinas (55)(56)(57). También se aprecia la gran variabilidad en el contenido de estos isómeros en las margarinas turcas (55)(58)(59) y pakistaníes (57). En relación a la margarinas griegas (60), aunque su contenido en *trans* es relativamente bajo, los autores indican una elevada cantidad de ácidos grasos saturados que discrepa con lo declarado en la etiqueta. Lo mismo ocurre en el estudio de Tekin *et al.* (58), ya que 4 de las 14 margarinas analizadas son "libres de *trans*", pero tienen elevadas cantidades de ácidos grasos saturados de cadena corta, lo que sugiere que han sido elaboradas con aceite de coco.

Tabla 3. Contenido promedio (expresado como % de ácidos grasos totales) de ácidos grasos *trans* en margarinas en la década del 2000.

C14:1t	C16:1t	C18:1t	C18:2t	C18:3t	Trans totales	País (Referencia)
-	-	-	-	-	1,60 0,30-3,70	Austria (57)
-	-	28,61	-	-	-	Argentina (81)
-	0,08 * 0,14† 0,22 *	2,54* 3,16† 14,60‡	1,96 * 2,20† 0,17‡	0,16 * 0,12† 0,14‡	5,20* 6,10† 15,20‡	Turquía (55)
-	-	8,18	0,49	0,21	8,87	España (65)
-	0,01	4,88	0,45	0,03	5,37	Alemania (61)
-	< 0,10	5,90	0,30	0,20	6,70	Escocia (62)
-	-	1,20* 9,70† 21,10‡	1,00* 1,00† 2,00‡	0,20*† ‡	2,40* 11,10† 23,40‡	USA (56)
-	-	2,00	0,50	0,01	2,50	Portugal (53)
-	-	-	-	-	0,0-37,8	Turquía (58)
-	-	-	-	-	0,01-19	Grecia (60)
-	-	0,40-27,4	-	-	0,90-32	Turquía (59)
-	-	2,00	0,10	-	2,50	España (54)
-	-	-	-	-	< 4,10* 1,6-23,1‡	Pakistán (57)

* Margarina blanda, † Margarina semiblanda, ‡ Margarina dura

En cuanto a los distintos isómeros *trans*, se verifica el predominio del C18:1t, seguido de C18:2t, como en décadas anteriores. Le siguen en cantidad C18:3t y C16:1t, mientras que no se detecta C14:1t. Algunos autores (61)(62) también identifican isómeros *trans* del C20:1 ó C22:1, proveniente de aceites de pescado hidrogenados.

En España, donde la dieta Mediterránea esta muy arraigada, es el país que muestra los menores niveles de muertes por enfermedad cardiovascular de toda Europa (63). Tradicionalmente el aceite de oliva es la mayor fuente grasa en dicha dieta, aunque ha habido un incremento gradual en la ingesta de margarinas y mantequillas en los últimos años. Aunque la ingesta de margarina en 2000 era aun baja (2,46 g/persona/día) la ingesta de alimentos que la contienen (bollería industrial, galletas, etc.) se ha incrementado (64). Puede decirse que en España la tendencia también es a reducir este tipo de ácidos grasos, ya que hasta 1996, con la excepción de las seis margarinas analizadas por Coll y Gutiérrez (35), el contenido de los mismos estaba por encima del 10%, reduciéndose a 8,87% en 2000 (65), hasta llegar al 2,50% actual (53) (Tabla 4). Todos estos estudios destacan la gran variabilidad de dichos ácidos grasos existente entre las muestras: entre 0,30% y 34,70%. Esta variabilidad puede explicarse por los distintos parámetros usados durante el proceso de fabricación, por ejemplo las condiciones de hidrogenación y/o desodorización (66), así como por la cantidad de ácidos grasos insaturados presentes en las materias primas usadas para la elaboración de estos productos (31). Henninger y Ulberth (67) afirman que la composición de las margarinas puede depender del precio que las materias primas tengan en el mercado. Otra razón de la variabilidad es la aparición de las margarinas llamadas "libres de *trans*". Una práctica utilizada para producir las llamadas "interesterificación", que es una alternativa al proceso de hidrogenación parcial que puede ser usada para conseguir aceites y grasas deseadas desde un punto de vista funcional. Consiste en una mezcla de aceites o grasas vegetales altamente saturadas (ej. aceite de palma o aceites totalmente hidrogenados) con aceites líquidos. Los niveles de ácidos grasos *trans* de las mezclas interesterificadas son muy bajos (0,10%), comparados con lo de las grasas de los alimentos comerciales (1,30% - 12,10%) (68).

Tabla 4. Contenido promedio o niveles máximos y mínimos(% de ácidos grasos totales) de ácidos grasos *trans* en margarinas españolas.

C18:1t	C18:2t	C18:3t	Trans totales	Referencias
0,1-32,7	0,05-1,48	-	10,79	36
6,4	0,24	-	6,68	35
2,38*	0,11*	-	2,55 *	
11,37	0,14		11,50	45
2,14*	0,00-0,01*		2,1 *	
-	-	-	10,80	71
-	-	-	16,80	75
8,18	0,49	0,21	8,87	65
2,00	0,10	-	2,50	54

* Margarina blanda

Los diversos estudios sobre los efectos desfavorables de los ácidos grasos *trans* parecen haber influido en los productores de margarinas, que han reducido las cantidades de estos isómeros en sus productos (42). En la [Tabla 4](#) se observa la tendencia a la reducción de los ácidos grasos *trans* en las margarinas españolas; la [Tabla 5](#) muestra la misma tendencia en países como Francia (69), Austria (67), Alemania (51, 61), Escocia (62) Dinamarca (70) y Estados Unidos (56); mientras que en Canadá (42), las margarinas siguen teniendo cantidades elevadas de estos ácidos grasos.

Tabla 5. Porcentaje de ácidos grasos *trans* en margarinas en distintos periodos

Años	C16:1t	C18:1t	C18:2t	C18:3t	Trans totales	País (Referencias)
1991	-	13,00	-	-	-	Francia (69)
1995	-	3,80	-	-	-	
1991/92	-	-	-	-	15,70	Austria (67)
1995	-	-	-	-	6,50	
1991	-	9,58	-	-	-	Alemania (51)
1995	-	4,62	-	-	-	
1994	0,03	20,71	1,00	0,00	21,77	Alemania (61)
1999	0,01	4,88	0,45	0,03	5,37	
1995	2,70	7,20	0,80	0,20	28,90	Escocia (62)
1998	< 0,10	5,90	0,30	0,20	6,70	
1991	-	1,90*	-	-	-	Dinamarca (70)
	-	9,80 †	-	-	-	
	-	5,80 ‡	-	-	-	
1995	-	1,30*	-	-	-	
	-	1,20 †	-	-	-	
	-	4,20 ‡	-	-	-	
1993	-	-	-	-	5,50*	USA (56)
	-	-	-	-	15,00 †	
	-	-	-	-	23,00 ‡	
1998	-	-	-	-	2,40*	
	-	-	-	-	11,10 †	
	-	-	-	-	23,40 ‡	

* Margarina blanda † Margarina semiblanda ‡ Margarina Dura

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