Chemical Interesterification of Palm, Palm Kernel and Coconut Oils

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ABSTRACT

Chemical interesterification processes are discussed as they apply to palm, palm kernel and coconut oils. Included are process descriptions, selected physical and functional changes resulting from this process, analytical techniques and commercial edible applications. These fats are utilized worldwide in a growing variety of food products. The demands of these applications provide an endless need for fats with varying physical and functional characteristics. Interesterification alone and in combination with other processes such as hydrogenation and fractionation significantly extends the range of the otherwise limited physical and functional characteristics of naturally occurring palm, palm kernel and coconut oils.

INTRODUCTION

Chemical interesterification, which alters the natural distribution of fatty acids in triglycerides and requires only heat and traces of alkaline catalyst, is of major importance to the edible oil industry in providing the physical and functional properties necessary to meet the challenges of today's food industry. While fatty acid rearrangement to total randomization is by far the most widely utilized adaptation, directed rearrangement also offers practical options. In reviewing and comparing examples of the randomization process, methods of reaction control and evaluation including melting point, solid fat profiles by dilatometry and pulsed nuclear magnetic resonance, glyceride analyses by gas liquid chromatography, and crystallization and melting profiles derived from differential scanning calorimetry are discussed in this paper. Selected melting point and solid fat content data are graphically presented to illustrate the changes in crystallization behavior resulting from randomization or directed interesterification of both partially hydrogenated and unhydrogenated palm, palm kernel and coconut oils. The versatility and functional impact of interesterification are further demonstrated through references to applications in cooking and frying oils, margarines and confectionery fats.

PROCESS DESCRIPTION

The basic objective of commercial interesterification is creation and concentration of glycerides with desirable physical and functional properties at the expense of those glycerides considered less desirable. Nature has given each type of oil a unique fatty acid composition and a particular distribution of fatty acids within the triglyceride molecules. Although the melting characteristics of individual fatty acids influence the melting characteristics of the triglycerides in which they are combined, the presence of a variety of fatty acids and orientations thereof in the triglyceride make for complex relationships which determine a fat's melting characteristics and crystalline properties. Interesterification, as it relates to the production of edible fats and oils, is a process where the orientation of fatty acids in the triglyceride molecules is rearranged. This rearrangement is effected in a random or directed manner. Either method often results in the synthesis of profoundly different triglyceride compositions in a predictable manner following the laws of probability. The interesterification reaction has been known since the ester interchange reaction reported by Friedel and Crafts in 1865 (1). In the 1930's, T. P. Hilditch and others observed that saturated and unsaturated fatty acids were not randomly distributed in most naturally occurring triglycerides (2). Others demonstrated that interesterified fat had a statistically predictable random fatty acid composition based on the composition of the starting triglycerides. This was clearly confirmed experimentally by reacting an equimolar mixture of tristearin and triolein (3,16). More recent work has proven experimentally that complex fat mixtures also conform to a pattern of random distribution following interesterification (17).

CATALYSTS

Although the ester-ester interchange may occur without the use of a catalyst at temperatures of 250 C and higher, the most common methods use alkali metal alkylates or alkali metals as catalysts. Fats reacted at high temperatures alone proceed to equilibrium slowly and, as a result, usually exhibit isomerization, polymerization, and decomposition (4). The alkali metal alkylate, sodium methylate, is a widely used rearrangement catalyst today. Like the alkaline metals, this catalyst is active at lower temperatures, speeds up the reaction, and does not require vacuum (5). It also has the additional advantages of being low cost and easily dispersed in fat.

Sodium-potassium alloy (Na/K) has also been used in the rearrangement process because it is liquid at ambient temperature and does not require dispersing in solvent prior to introduction to a reactor, as is true for Na and K metals. As shown in Figure 1, the lowest melting Na/K alloy has a freezing point of −12.3 C (6). Although typically more costly, Na/K alloy is much faster at catalyzing the interesterification reaction at lower temperatures than Na or K or either alkylate (7). This is apparently due to the ability of the liquid Na/K particles to maintain unreacted metal on their surfaces while solid particles of Na, K, or their alkylates become coated with oxides and hydroxides (8). Although Na/K alloy can be directly dispersed in triglyceride blends, a high sheer agitator is sometimes recommended to assure fine particle formation and distribution.

The lowest cost catalysts are alkaline hydroxides, NaOH and KOH. Used in combination with glycerol, these catalysts have the disadvantages of requiring a two-stage reaction under vacuum and higher temperatures to effect rearrangement. The first stage is conducted at near 60 C to neutralize any free fatty acids, remove traces of moisture, and disperse the catalyst. The second stage moves to higher temperatures (140-160 C) to effect rearrangement (9).

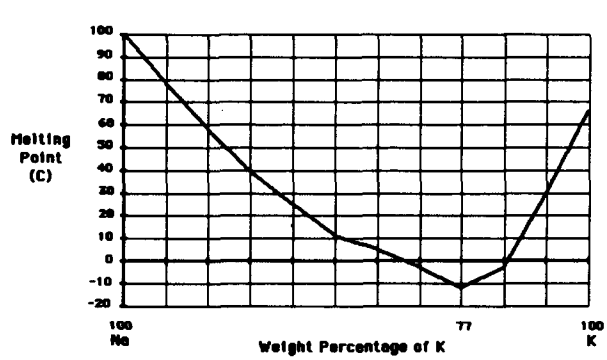

FIG. 1. Na/K phase diagram (6).

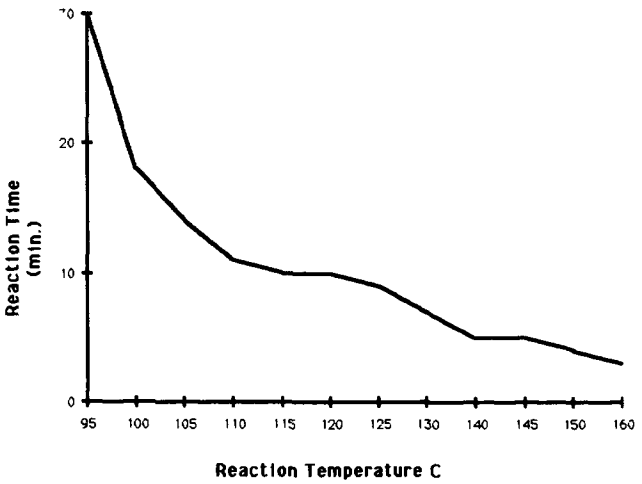

FIG. 2. Plot of reaction time vs. temperature for glycerol/NaOH interesterification.

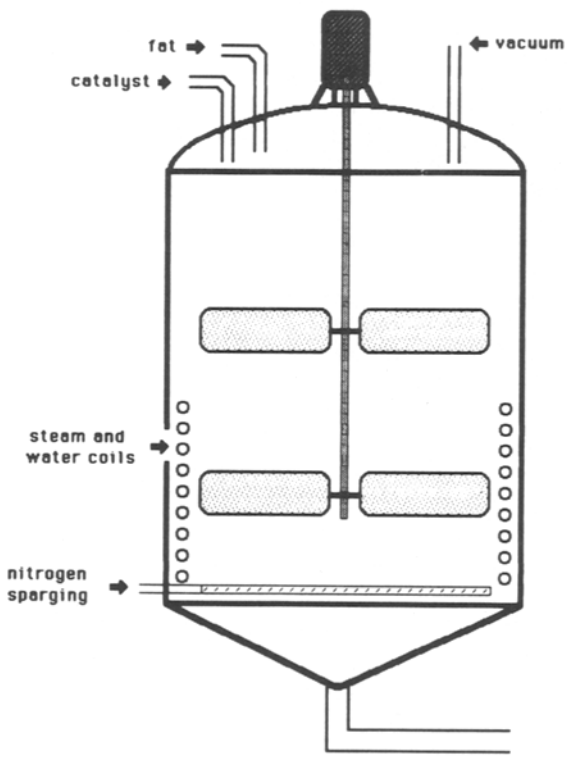

FIG. 3. Typical batch reaction vessel for interesterification (14,15).

Figure 2 shows the influence of temperature on rate of reaction.

In reality the above compounds likely serve only as initiators in the process of forming the true interesterification catalyst. Two possible mechanisms of formation have been suggested in the literature (10,11). Most likely an intermediate glycerate anion is formed and serves as the active catalyst (12,13). The characteristic brown color that develops in a catalyzed interesterification reaction is reported to be associated with the formation of this active catalyst (14). Once this color has formed, the remainder of the reaction proceeds rapidly to complete randomization unless directed otherwise.

RANDOM REARRANGEMENT

Random rearrangement is accomplished with either batch or continuous methods. A typical batch reaction vessel fitted with an agitator, heating/cooling coils, N_2 sparging, and vacuum is shown in Figure 3. Initially, in a batch process, the fat or fat blend is heated to 120-150 C in the reaction vessel while under vacuum (14,15). This drying step is critical since moisture is most effective at deactivating the catalyst. In fact, moisture levels in excess of 0.01% and/or free fatty acid levels in excess of 0.05% require increased levels of catalyst to compensate for their poisoning effects. Ideally, once the fat is well dried, only 0.1% sodium methylate is necessary to promote the interesterification reaction. In practice, average usage levels of sodium methylate may range from 0.2% to 0.4% (14). The addition of each additional 0.1% catalyst is likely to result in a neutral oil loss of about 1% following catalyst neutralization, refining, and deodorization (15).

Following the drying step, the mixture is cooled to reaction temperatures ranging from 70-100 C. Sodium methylate powder is then sucked into the reaction vessel and is well dispersed to form a white slurry (some procedures would precede this step with the addition of small amounts of soda ash to neutralize most free fatty acids). The oil/catalyst slurry is well agitated 30-60 min. until formation of the distinctive brown color denoting randomization. Once completion of reaction is confirmed by laboratory analyses, the catalyst is often neutralized in the same reaction vessel (12). Neutralization may include the addition of CO_2 (18) or phosphoric acid prior to water washing, refining, and drying. When water combines with sodium methylate, sodium hydroxide and methyl alcohol form. Both will react with neutral oil to form soap and methyl esters. By keeping catalyst usage to a minimum and neutralizing with phosphoric acid or CO_2 prior to water addition, processing losses may be kept to a minimum.

Continuous random rearrangement processes are well described in the literature (14,15,19). In these descriptions the fats are flash dried, catalyst is continuously added, and the mixture is passed through elongated reactor coils with variable residence time determined by length and flow rate. The catalyst is then neutralized with water and passes on to centrifugal separation and drying.

When the random rearrangement process is to be combined with partial hydrogenation, it is often desirable to interesterify prior to hydrogenation. By doing so, free fatty acid levels less than 0.1% are probable. Less catalyst will be required and lower losses will result. Moreover, the final melting endpoint is better controlled in the hydrogenation process and the fat may be sent directly to the deodorizer from the hydrogenation plant with less chance of commingling with other oils. Technically, hydrogenation prior to rearrangement alters the fatty acid composition and thus influences the final random distribution following randomization. In practice, however, physical and functional results are nearly identical.

DIRECTED REARRANGEMENT

In directed rearrangement processes, one or more of the triglyceride products of the interesterification reaction is selectively removed from the ongoing reaction. Once these components are removed, the reaction balance is disturbed and the remaining reactants continue to rerandomize, thus favoring continued formation of specific glycerides. Typically, the degree of saturation and/or molecular weight are most important in determining mode of removal. Some procedures involve continuous distillation of low molecular weight acids (15). A more common procedure involves the selective crystallization of higher melting, more saturated triglycerides (5,20). That is, as trisaturates crystallize

out of reaction, the remaining liquid phase will continue further rerandomization, thus forming more trisaturates.

Na/K alloy is often sighted as the catalyst of choice for directed rearrangement because of its superior activity at relatively low reaction temperatures (12,21). Typically, Na/K is metered in by pump at about a 0.2% level and well dispersed using a high sheer agitator to provide the proper catalyst particle size necessary to assure high activity (12, 14). Initially the fat is at least partially randomized at temperatures above the point at which all its triglycerides remain liquid. When utilizing the fractional crystallization approach, the fat/catalyst slurry is then chilled in conventional scraped-wall heat exchangers to specific temperatures in a series of steps designed to maintain the directed fractional crystallization process. Once chilled, the mixture is held for a period of time under gentle agitation to achieve the desired degree of crystal formation. Enhancements of this procedure now include both the stepwise reduction of temperature (20,24) and the use of high- and low-temperature cycles to raise overall yield of saturated triglycerides and accelerate reaction times (22,23). Upon completion the catalyst is neutralized with water prior to heating and refining.

EFFECTS OF INTERESTERIFICATION ON PALM KERNEL, COCONUT AND PALM OILS

The dropping points of interesterified palm, palm kernel and coconut oils are presented in Table I. The significant reduction in dropping point reported for saturated rearranged palm kernel oil (saturated random Rx PKO) and saturated rearranged coconut oil (saturated random Rx coconut oil) is due to an increase of triglycerides with a lower average molecular weight. The reduction in dropping point reported for randomized PKO is likely due to an increase of triglycerides with intermediate degrees of unsaturation (17). Palm oil increases in melting point upon random rearrangement due to a rise in fully saturated triglycerides. The solid fat content profiles of a palm oil, randomized palm oil and directed rearranged palm oil are shown in Figure 4 along with the resulting levels of saturated (S3) and unsaturated (U3) triglycerides (15). As shown, complete randomization of this palm oil produces only modest changes in the solid fat profile. Directed rearrangement, on the other hand, produces more significant increases in solid fat contents (SFC) at higher temperatures. It is apparent that this boost in SFC is again due in large part to the rise in S3 triglycerides. Table II shows SFC profiles of saturated palm kernel and coconut oil compared to their saturated randomized counterparts.

Interesterification not only alters the melting characteristics of these oils but may also influence crystal morphology and rate of crystal formation. It has been observed for many years that these oils crystallize slowly and are, as a

TABLE I

Dropping Point Data Following Interesterification (°C)[a]

	Before Rx	Random Rx	Directed Rx[b]
Palm oil	39.4	42.7	51.1
Palm kernel oil	28.3	26.9	30.0
Coconut oil	25.5	28.2	–
Saturated palm kernel oil	45.0	34.4	–
Saturated coconut oil	37.8	31.6	–

[a]Data generated using Mettler FP80/FP83 automatic dropping point apparatus.

[b]Directed rearrangement conducted using sodium methylate as catalyst. Catalyst/fat slurry cooled to 68-70 F and held for 48 hr prior to neutralization.

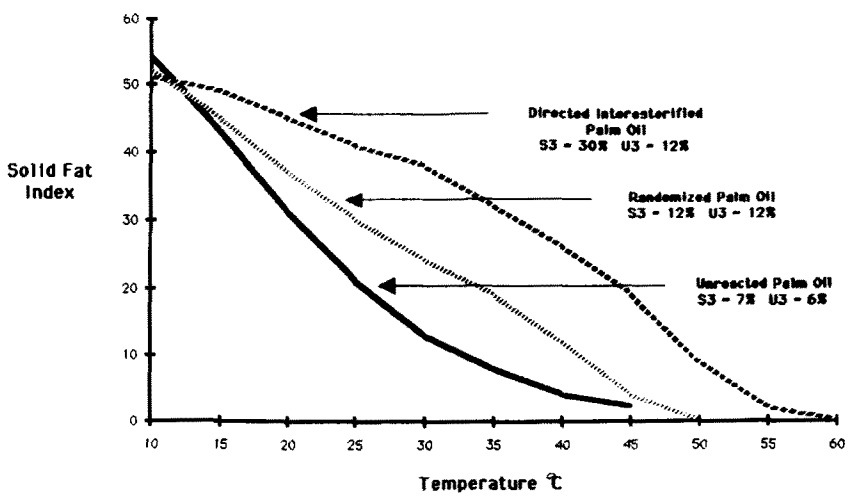

FIG. 4. Solid fat index profiles of palm oil, randomized palm oil, and directed interesterified palm oil along with resulting levels of saturated (S3) and unsaturated (U3) triglycerides (15).

TABLE II

Changes in SFC Profiles Due to Random Interesterification of Hydrogenated Palm Kernel and Coconut Oils

Percent solid fat content by NMR @	Hydro PKO	Hydro Rx PKO	Hydro coconut	Hydro Rx coconut
10.0 C	89.9	85.0	84.8	70.1
21.1 C	79.2	63.8	46.3	39.3
26.7 C	53.4	39.1	10.1	16.4
33.3 C	19.9	11.2	3.1	0
37.8 C	7.4	0	0	0

result, often difficult to chill and package. Immediately following packaging the product may be too soft. Later following completion of crystal growth, the product may become much too hard. During storage, palm oil-based blends may also develop grainy crystal aggregates contributing to undesirable organoleptic qualities (25-27). Following corandomization of selected fat blends, these undesirable characteristics are often reduced or eliminated.

ANALYTICAL METHODS OF EVALUATION

The interesterification reaction is most often confirmed in commercial operations by closely monitoring changes in color, melting point, and solid fat content profiles. Certainly the quickest techniques involve looking for the development of the characteristic brown color and checking for specific changes in melting point. These quick checks are only effective, however, when an easily measurable increase or decrease in melting point can be expected. The brown color development alone is not sufficient to confirm completion of reaction since it develops at the onset of the rearrangement reaction. Complete rearrangement follows after a period of time which is dependent on such factors as choice of catalyst, reaction temperature, quality of oil, etc. Other analytical methods are now commonly employed to assess reaction progress and final results. Principle among these are solid fat content by dilatometry or pulsed nuclear magnetic resonance (NMR), differential thermal analysis by differential scanning calorimetry (DSC), and triglyceride analysis by high performance liquid chromatography (HPLC), thin layer chromatography (TLC), and gas liquid chromatography (GLC).

Small changes in melting point may be accompanied by more significant changes in solid fat content throughout a range of functionally important temperatures. For many years a dilatometric method of analysis has prevailed. In recent years solid fat content analysis by NMR has gained increasing acceptance as a rapid, accurate technique of measurement (28). The chromatographic methods now available separate triglycerides according to their level of saturation or on the basis of molecular weight. Shown in Table III are triglyceride carbon number analyses by GLC of Malayan palm kernel oil and interesterified palm kernel oil along with the calculated composition of randomized palm kernel oil (29). HPLC separation of triglycerides using reverse phase chromatography is well reported in the literature (30,31). Separation of the triglycerides of palm kernel and coconut oils according to degree of unsaturation and molecular weight is easily accomplished by this method (30) and serves as a useful tool in studying the changes in

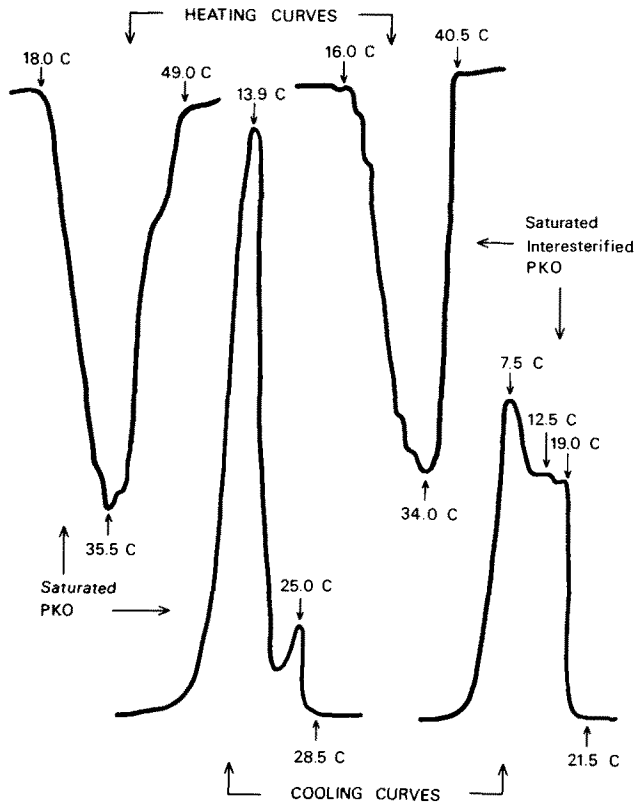

FIG. 5. Comparison of heating and cooling thermograms by differential scanning calorimetry of saturated palm kernel oil (PKO) and saturated interesterified PKO.

structure and behavior resulting from interesterification. Differential scanning calorimetry is most useful in studying the kinetics of crystallization and melting of triglyceride mixtures under dynamic conditions, thus supplementing measurements derived from NMR and various melting point techniques. The heating and cooling thermograms resulting from DSC show distinct differences between some nonrandomized and randomized oils. Figure 5 compares saturated palm kernel oil with saturated interesterified palm kernel oil. Differences shown between the cooling thermograms may be most dependent on the influence of spontaneous crystallization following supercooling. Triglyceride composition and polymorphism may be less significant (29). Therefore, it is important to study samples under a variety of rates of temperature change to generate comprehensive DSC studies (32).

TABLE III

Triglyceride Carbon Number Analyses by GLC (29)

Triglyceride carbon no.	Malayan palm kernel oil	Interesterified palm kernel oil	Calculated composition of randomized palm kernel oil
32	6.6	5.2	1.1
34	8.6	5.9	6.7
36	21.1	16.4	16.8
38	16.8	16.2	14.7
40	9.6	12.7	14.9
42	9.2	18.6	19.3
44	6.8	10.4	10.5
46	5.5	5.8	6.7
48	6.5	5.7	6.2
50	3.0	1.8	1.8
52	3.2	0.8	0.8
54	3.6	0.6	0.5

TABLE IV

Interesterified Hard Butters Made From Partially Hydrogenated Palm Kernel, Coconut, and Palm Oils (Typical Properties)

Wiley melting point[a]	35.0 C	36.6 C	38.9 C	42.2 C	44.4 C
Iodine value[b]	2.0	2.0	2.0	2.0	2.0
Solid fat index[c]					
@ 10.0 C	64	65	66	66	68
21.1 C	52	54	54	56	59
26.7 C	37	39	40	45	49
33.3 C	8	10	14	19	26
37.8 C	0	0	3	9	14

[a]Wiley melting point by AOCS method Cc 2-38.
[b]Iodine value by AOCS method Cd 1-25.
[c]Solid fat index by AOCS method Cd 10-57.

COMMERCIAL APPLICATIONS UTILIZING PALM, PALM KERNEL AND COCONUT OILS

Commercially, the interesterification process is regularly used in processing palm, palm kernel and coconut oils to produce a variety of margarines, cooking and frying oils, and confectionery fats. Most often interesterification is combined with other specialized processing techniques such as hydrogenation and/or fractionation. By combining interesterification with these and other more sophisticated techniques, the fatty acid and glyceride composition can be manipulated to achieve the most desirable physical and functional properties. Moreover, these oils are often combined with other carefully selected fats. These blends of course vary according to the type of end product desired.

The incorporation of palm and lauric oils in margarines and reduced calorie spreads has relied heavily on the interesterification process. As mentioned earlier, these fats have displayed a tendency to crystallize slowly and later to become quite hard during storage. Certainly these characteristics are undesirable in margarine products for both the processor and the end user. The patent literature describes numerous approaches utilizing interesterification to address these concerns.

Nelson described a process where lard and coconut oil were corandomized to produce a margarine oil with desirable crystalline and melting properties (33). Wieske, Kattenberg and others have described the production of margarine oils containing significant levels of interesterified palm and lauric oils in combination with other fats to achieve rapid crystallization properties while maintaining desirable spreadability and mouth feel characteristics (26,27,34,35). Ward and others have described margarine oils of particular nutritional interest composed of hydrogenated interesterified palm and lauric oils in combination with highly unsaturated oils. These formulations are high in polyunsaturates and very low in *trans* isomer content (36,37). Reed, Carlile and others have patented margarine oil formulations containing from 20 to 60% interesterified palm oil that are particularly well suited for soft tube margarines which can be spread directly from the refrigerator (38,39).

Interesterified palm oils also find application in cooking, frying, and salad oils. Once again palm oil's posthardening property may be averted through interesterification and corandomization with other fats and oils. By combining fractional crystallization and directed interesterification, a number of useful palm oil products may be produced including a fluid salad oil fraction (40). Typically the lauric fats find only limited use in these applications because of a variety of factors including relatively low smoke points, a susceptibility to hydrolysis in the presence of water and lipolytic enzymes, and a tendency to produce foaming when combined with other nonlauric oils (41).

The formulation of confectionery and other specialty fats, commonly called hard butters, offers a great variety of applications for interesterification processes (42-45). These fats, often used as total substitutes for cocoa butter in confectionery coatings and other applications, are characterized by relatively high solid fat content at ambient temperatures as well as a rapid melt down in the mouth. These qualities result in confections with hard, dry textures at room temperatures and excellent flavor release upon eating. Typically, interesterified hard butters are substantially composed of randomized and corandomized, hydrogenated palm kernel and coconut oils in combination with lesser quantities of such fats as palm oil, cottonseed oil or soybean oil. By blending these ingredients in selected proportions, a whole series of excellent hard butters is obtained with melting points typically ranging from 35 to 45 C. Table IV lists some typical properties of a group of interesterified, hydrogenated blends of palm kernel, coconut and palm oils regularly used in confectionery applications.

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Session VII discussion

The following questions, answers and comments were presented during the informal discussion held at the conclusion of Session VII.

Q: The slow crystallization rate of palm oil, i.e. 27 minutes at 20 C, was mentioned. What would be the crystallization rate for palm mid-fraction (PMF) which has a substantial portion of the POO group removed, leaving POP in its composition?

Young: I have no first hand experience, but from a more general experience I would expect little change in the rate of crystallization between palm oil and palm mid-fraction. The main effect (increasing rate) is obtained by hydrogenation.

Q: The rate of crystallization usually is defined in terms of units/time. What units are you using in your slide showing crystallization rates of different oils?

Young: The purpose of the table shown was to draw attention to changes in residence time in tube chillers required with changes in oil blend constituents. See J. Madsen, Grindsted Products, for further detail.

Q: Do you know of any commercially available computer program for the linear programming optimization of oil blends?

Young: To the best of my knowledge, there is no such program available.

Q: Are fat least cost blending programs (software) commercially available? If so, from who? I am interested in seeing a list of the parameters selected and their relative values.

Young: There are no commercially available programs due to the small market. The programs in use are written by the users themselves. The parameters include all the points listed in the lecture, e.g. including legislation factor.

Comment, Ralph Timms: The questioner is referred to a book by Dover Publications on "Linear Regression for Food Systems."

Q: What are the crystal inhibitors available and how do they prevent crystal formation in oils?

Young: Crystal inhibitors include oxystearin and dihydroxy stearin.

Q: Currently we are studying the fermentation technique to modify the structure of oils and fats. We are therefore most excited to hear of your dehydrogenation process to modify oils and fats. Could you elaborate on how this process might be developed?

Young: The dehydrogenation process is a prospect for the future. Regretfully, there is no such process at present.

Q: Will 2-nitropropane be banned in the United Kingdom and Scandinavia as well as the European Economic Community?

Young: It will be banned in the United Kingdom and Denmark. For the rest of Scandinavia, the answer is no, but it will be affected by the EEC legislation.

Q: In your lecture you mentioned that legislation is one of the obstacles to the interchangeability of oils and fats. Does this apply to other countries around the world?

Young: Yes. For example, palm oil is not allowed for edible use in Iraq.

Q: Referring to fractional crystallization using solvent, which of the four solvents mentioned is the most suitable for the fractionation of cocoa butter substitute? Can you comment on the minimum reported solvent ratio and the maximum reported commercially obtained yield? The basis is the CBS of impeccable quality. In Table III you presented crystallization times at different transformation temperatures for different oils. What would be the influence of solvents on both transformation temperature and crystallization times?

Timms: The use of solvent helps to speed up the rate of crystallization and increases the crystallization temperature. As for the choice of solvent, the questioner is referred to one of my previous papers on this subject (ISP/PORIM 1981, Conference in Kuala Lumpur).

Q: Do you think there is going to be homogeneous catalyst for oil in the near future?

Young: Unless the cost is reasonable and the effect is different compared to the present, this technique is only for the future, as it would add to the capital cost of equipment required for catalyst removal.

Q: Regarding the microbial interesterification of palm oil using 1,3-specific lipases, what type of bed-reactor would you suggest—Kiesulguhr, Celite, etc.? There is also a problem of melting point with the above that would not be applicable for an emulsion system. What system would you recommend?

Young: First, the questioner is referred to a Unilever patent (Macrae) or the article by Macrae in JAOCS (lecture given at the Hague conference, October 1982 and published in JAOCS 1983 February issue). Second, I am sorry that I cannot help you with this inquiry on an emulsion system.

Q: May I know the type of HPLC column and the chromatographic conditions used to separate the triglycerides in palm stearin and other palm oil fraction? Where do you obtain your triglyceride standards?

Deffense: HPLC conditions used in this paper are two columns in series, a micro-Bonapak C78, 5 μ Waters and a Lichrosorb Rp-18, 5 μ Merck; and a Waters delivery pump 6000 A, with a septumless loop injector UCK. The detector used is a Waters R 407 differential refractometer. Palm oil and palm oil stearin and olein were run isocritically at 50 C using a mixture of acetone-acetonitrile (62.5:37.5); palm mid-fractions were eluted at 40 C. For more details see the paper, "Analytical Data of End Products through HPLC," published in JAOCS 60:474 (1983) and the full paper published in a French journal "High Performance Liquid Chromatographic Analysis of Triglycerides and their Fractions Obtained by Fractional Crystallization in Vegetable and Animal Fats," Review Francaise CORPS GRAS, 37:123 (1984). Triglyceride standards were obtained from Supelco, Fluka and synthesis.

Q: What happens to the rate of diglycerides during the fractionation of palm oil described by you?

Deffense: The diglycerides migrate mainly to the olein.

Q: Would the speakers on interchangeability and fractionation discuss in more detail the effect of partial glycerides, particularly diglycerides, on the efficiency of the fractionation process and on product quality?

Deffense: Concerning the effect of diglyceride on the efficiency of the fractionation process, three points should be mentioned. As mentioned in the lecture presented by Dr. Timms, the diglycerides make an eutectic with triglycerides. It was shown by many authors that the addition of diglycerides to palm oil decreases the slip melting point and the SFC. As a result they delay the crystallization. As palm oil contains only around 6% diglycerides the first effect is not generally observed. On the contrary what we observe sometimes is that the high melting point diglycerides have an effect of seeding making nuclei. As a result the crystallization starts earlier giving crystals of smaller size but quite filter-

able. Such effect is clearly shown in the case of cocoa butter where the addition of diglycerides to cocoa butter speeds the rate of crystallization. A third point concerning the diglycerides' effect is their effect on the polymorphism; please refer to a recent dissertation presented by Dr. Hernguint in Sweden a few months ago. It was shown that rapeseed oil which crystallized in the β form can be stabilized in the β prime form where 2 to 3% of diglycerides are added to rapeseed oil, especially the 1,2 diglyceride when palm oil is crystallized at high temperature where the polymorphism transitions are critical, the diglycerides may stabilize the β prime form. Effect of diglycerides on product quality? If the speaker means olein quality, I would say that the diglycerides have a detrimental effect on the cold stability temperature. Here is an example storing two oleins containing around 6% diglyceride when obtained by dry fractionation and the other one having around 9% diglycerides when obtained by solvent crystallization. The last olein contains more unsaturated and less saturated triglycerides than the olein from dry fractionation. However, its cloud point is around 6 C instead of around 5 C, i.e. one degree higher.

Q: Could you please throw some light on the effect of minor impurities carried with the feedstock on the overall fractionation effect? Even ppm range of certain impurities can affect both nucleation and crystal growth, so that within a prescribed residence time the batch experiences a different history of initial supersaturation levels and of crystal deposition both in terms of crystal form and crystal growth rate. How do you cope with these problems?

Deffense: Generally the phospholipids, monoglycerides, cellulose and pectins have a detrimental effect on the crystallization. As a result crystals of different size are obtained. If cellulose and pectins, for example, are removed by an enzyme treatment (see Tirtiaux patent) we obtain a much better crystallization.

Q: In the Tirtiaux fractionation process, do you find a rise in the level of oxidation in the oil due to air drawn through the filter cake while it is passing over the vacuum filter?

Deffense: When palm oil is crystallized and filtered through the vacuum florentine filter we do not observe an increase of peroxide value. However, for long storage we recommend deaerating the olein, which contains a lot of air.

Q: What is the best filter for palm oil mid-fraction? What are typical yields for best systems?

Deffense: For commercial PMF obtained from a Tirtiaux plant, depending on the feedstock quality, an average yield of 30 to 25% is obtained.

Q: Could you give some information about dry crystallization time and temperature of palm kernel oil?

Rossell: Temperature is the same as detergent process.

Q: We have observed that in many applications palm kernel olein (or coconut olein) which is hydrogenated has superior crystallization behavior in terms of crystal size, compatibility, etc. over palm kernel or coconut stearin. Could you please comment on that?

Rossell: This could be due to the higher melting point and lower amount of lauric acid content.

Q: You indicated difficulty in disposing of palm kernel olein in that the palm kernel stearin is used mostly for food. Have you considered diverting the palm kernel olein to the oleochemical industry for processing into fatty alcohols or acids? Is this idea practical?

Rossell: It is not economical to use food grade palm kernel olein for the oleochemical industry.

Q: In your paper, you have indicated that using wet detergent process, the palm kernel stearin yield is about 40% when palm kernel oil with an IV of 18.3 is fractionated at 25 C. Is the palm kernel stearin yield figure from a commercial plant? What do you think the palm kernel stearin yield will be if a crude palm kernel oil with IV of 17 is fractionated at 25 C in wet process?

Rossell: I am not in a position to comment on this.

Q: You mentioned fractionation by solvent crystallization as a means of obtaining CBS. How many technologies are available commercially for this duty? Again the basis is first class products with a yield leaving nothing to be desired? In your presentation you assign low crystal growth rate to high mother liquor viscosity. If this is right, crystal growth rates will be of the order 10^{-5} m/s. However, reported crystal growth rates (also for fats) are of the order 10^{-8} m/s, implying interaction and control of at least one more process: surface integration. Why are you so sure that crystal growth rate is mass transfer controlled?

Rossell: See the paper by Jan Rek on fractionation that is referenced in my paper.

Q: You talked about the free fatty acid content in Malaysian and Nigerian palm kernel oil. How about diglycerides?

Rossell: The diglycerides are linked to the FFA content, hence the yield will be lower.

Q: During the crystallization have you been able to estimate the size of crystals?

Rossell: No.

Q: Instead of diluting palm kernel oil to about 20% solid content before separation, can the olein be double fractionated to increase the stearin yield? If the answer is yes, what are the quality differences between first fraction stearin and second fraction stearin, and what are the respective fractionation temperatures?

Rossell: I have no experience with this.

Q: What is the magnesium sulphate concentration in the detergent solution, and what is the fractionation temperature at the stage to separate detergent and stearin?

Rossell: 1% concentration and temperature of 45-50 C.

Q: Are there especially selective catalysts known for hydrogenation of fatty acids at 1,3 position of triglycerides?

Grothues: It would be ideal, but no.

Q: You mentioned that in the U.S. the reuse of catalyst has become obsolete. Can you please elaborate why it has become so?

Grothues: To my knowledge, as a result of using a very small amount of catalysts to produce the so-called soft and hard stocks which are used for making special blends.

Q: With your experience, please comment on the selectivity of Buss loop reactor as compared to conventional agitating type of reactor for the hydrogenation of palm and lauric oils.

Grothues: The S_i-selectivity is slightly lower than with stirrer equipped reactors, particularly the flat blade type. This can be counteracted by low H_2-pressure, probably by N_2 dilution, and so extend the hydrogen time. For laurics, normally no high selectivity is required.

Q: You discussed the different techniques for hardening palm oil to 45 C melting point and you demonstrated the difference in solid fat indices for S_I-selectivity compared to S_i-selectivity. Could you please comment on the level of *trans* isomers in each case?

Grothues: As to my memory, the actual figures are not with me; with S_I-selectivity we have some 40% and with S_i-selectivity some 60% of *trans* double bonds.

Q: In normal hydrogenation, would the reuse of spent nickel catalyst in conjunction with fresh nickel catalyst in the ratio 1:1 lead to a big increase of *trans* isomer of the hydrogenated product (e.g. hardened palm oil to an IV of 45)?

Grothues: It depends mostly on temperature. I would recommend no or only up to 10% of used catalyst.

Q: Besides the nickel catalyst, are there any other types of commercial heterogenous catalyst (which would reduce the risk of catalyst traces remaining in the final filtered hydrogenated product)?

Grothues: No.

Q: For interesterification of lauric palm blends what is the typical washing loss, the typical deodorizing loss and analytical plant control method, and how long will it take?

Young: Washing loss is about 2%; deodorizing loss is 0.5 to 1.0%. But ensure that good feed oil is used and careful control of conditions.

Pease: In lauric oils and blends of lauric oils and palm oil, melting point or drop point analysis is usually sufficient. However, on blends which result in small changes in melting point after interesterification, cooling curves or solid fat index evaluations are used.

Q: What is your experience with powder alkoxides catalyst and with caustic soda-glycerol-water catalyst system in the interesterification of both random and directed types of palm oil and its fractions with respect to slip point and SFI?

Young: Should be no difference.

Q: What is the scope of the interesterification reactions in the miscella phase?

Answer: Possible but so far as the panel knows is not technically carried out. Temperature must be at least above the melting point of highest melting triglycerides.