

# Monitoring Chemical Interesterification<sup>1</sup>

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**ABSTRACT:** Chemical interesterification has long been used to modify oils and fats into functional products. Many chemical compounds can be used as the catalysts, such as sodium metal and sodium methoxide. With addition of the catalyst, the oil turns a well documented distinctive reddish brown. Many believe that this color compound may be the real catalyst in interesterification. The spectral changes of an oil undergoing interesterification were examined in the visible and ultraviolet wavelength ranges. An absorbance peak was found from 320–450 nm. Because this range is the wavelength of blue light, this absorption gives the oil a reddish brown color, the compensated color of blue light. The peak increases as the amount of sodium methoxide increases. To initiate and complete interesterification, the oil absorbance must reach levels of 0.4 and 1.0 at 374 nm, respectively. Controlled partial interesterification is now also possible by controlling the absorbance between 0.4 and 1.0. A novel patent-pending technology, based on this observation, was developed to monitor the progress of interesterification on-line using fiber optic technology. The reaction time and the dosage of sodium methoxide used for randomization have been significantly reduced on bench-scale when using this new tool. Furthermore, the oils interesterified with monitoring have higher oxidative stability and tocopherol contents compared to those by conventional randomization.

Paper no. J9025 in *JAOCS* 76, 783–787 (July 1999).

**KEY WORDS:** Color, fiber optic, interesterification, mechanism, monitor, partial interesterification, plastic fats, randomization, sodium methoxide.

Chemical interesterification is an important process for the oils and fats industry. This reaction modifies the physical properties of oils by rearranging the distribution of fatty acids on the glycerol backbone without changing their chemical composition. This method was widely used in the United States in the 1950s and 1960s for lard crystal modification (1,2). With the rising concerns over the nutritional impact of *trans* fatty acids on health, interesterification may become more popular for preparation of low or zero *trans* functional plastic fats in the future.

There are two basic types of chemical interesterification: random and direct (3). In random interesterification, the reaction is initiated and completed at temperatures above the

melting points of the components. Under such conditions, interesterification will rearrange all of the fatty acids into a random pattern on the glycerol backbone after thermodynamic equilibrium is achieved. If interesterification is conducted at low temperature so that some fats with high melting points are crystallized, the oils in the liquid phase will then reach a new thermodynamic equilibrium. The crystallized fats will not be involved in interesterification because they are separated from the reaction phase. This practice is known as direct interesterification. Random interesterification is most commonly used in food industry to prepare functional plastic fats by interesterifying liquid oils such as soybean or canola oil with hard fats such as fully hydrogenated soybean oil or palm stearine.

Chemical interesterification can be induced by chemical catalysts including alkali metals, alcoholates, and sodium hydroxide with glycerol (3). One of the most commonly used catalysts is sodium methoxide. These catalysts have been shown actually to be precatalysts that react with triglycerides to produce the real catalyst intermediate. With the addition of these precatalysts, a reddish-brown color appears indicating the successful initiation of interesterification. Two types of catalytic reaction mechanisms have been suggested to explain chemical interesterification. Weiss *et al.* (1) suggested that the reaction starts when sodium methoxide attacks the  $\alpha$ -hydrogen of an acyl group to form the enolate ion. The enolate ion then reacts with another ester to form a  $\beta$ -keto ester. This is also referred to as the Claisen mechanism.

Another hypothesis (4) suggests that the methoxide ion attacks the carbonyl group directly and forms a diglyceride anion that functions as the real catalyst and transfers acyl groups around the glyceride backbones. Both mechanisms result in the formation of diglyceride ions. The difference between these two mechanisms is the donor of an acyl group for transesterification of the diglyceride ion. The first mechanism suggests that both  $\beta$ -keto and acyl esters are the donors for acyl transesterification. The second one proposes that acyl esters are the donor. Nonetheless, neither mechanism explains why the oils change color to reddish brown with addition of precatalysts during interesterification (3,5).

Intesterification is normally initiated at 70–120°C by 0.05–0.5% sodium methoxide after the oil has been completely dried. The oil quality and the efficiency of the drying system used play critical roles in determining the dosage of sodium methoxide. This catalyst is very reactive to moisture, free fatty acids, and peroxide substances in the oil. Typically,

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<sup>1</sup>Presented at the 89th American Oil Chemists' Society Annual Meeting, Chicago, IL, May 10–13, 1998.

**TABLE 1**  
The Fatty Acid Compositions of Experimental Oils

Fatty acids	High-oleic canola oil	Palm oil	Soybean oil	Soy stearine	Tallow
16:0	3.8	44.0	10.3	10.6	23.0
18:0	2.7	4.4	4.1	86.4	15.8
18:1	76.6	39.3	23.1	1.0	44.6
18:2	11.0	9.7	53.1	0.3	3.7
18:3	2.7	0.3	7.8	0.0	0.3
Others	3.2	2.4	1.6	1.8	3.5
Total <i>trans</i>	1.1	0.5	0.3	0.5	9.4

interesterification is conducted with high enough doses of catalyst and sufficient time to ensure complete reaction. Various postreaction tests including solid fat index, melting point, and sterol profile are often used to verify the completion of reaction. These off-line tests are both time- and labor-consuming. An on-line method would eliminate the need for such testing and certainly increase the productivity and reduce the cost of interesterification.

This paper describes a novel patent-pending method that is based on a quantitative measurement of oil spectral change after the addition of sodium methoxide during interesterification. This technology can monitor interesterification on-line with a fiber optic spectrometer, track the progress of interesterification reaction, and minimize the dosage of sodium methoxide and reaction time. Partial interesterification can also be carried out using this on-line monitoring technology. Partially interesterified products have unique functional properties (melting point and solid fat index/content) compared to the physical and randomized blends. Some of these products can be used directly as functional plastic fat ingredients.

## EXPERIMENTAL PROCEDURES

**Sodium methoxide.** Sodium methoxide (25 wt%) in methanol was purchased from Agros Organics (Pittsburgh, PA). Solid sodium methoxide was freshly prepared from this solution by evaporating methanol and grinding the solids to a fine powder before adding them to the oil.

**Oils and fats.** High-oleic canola oil, palm oil, soybean oil, and fully hydrogenated soybean oil (soy stearine, iodine value <5) were obtained from Cargill Oilseeds Division. Tallow was a product of Cargill Excel Division. Table 1 shows the fatty acid compositions of these oils used for interesterification.

**Intesterification.** Specific blends of oils were mixed and dried at 110°C under 10 mm Hg vacuum for 60 min, then up to 0.5% (w/w) of sodium methoxide fine powder was added to the dried oil blends to initiate interesterification. Samples were taken at various intervals and their spectra were recorded. The sampled oils were mixed in a 1:10 ratio with hexane containing 1% acetic acid. The solutions were then filtered through Whatman #4 filter paper (Whatman International Ltd., Maidstone, England). The solvents in the filtrates were completely evaporated on a steam bath with a nitrogen stream.

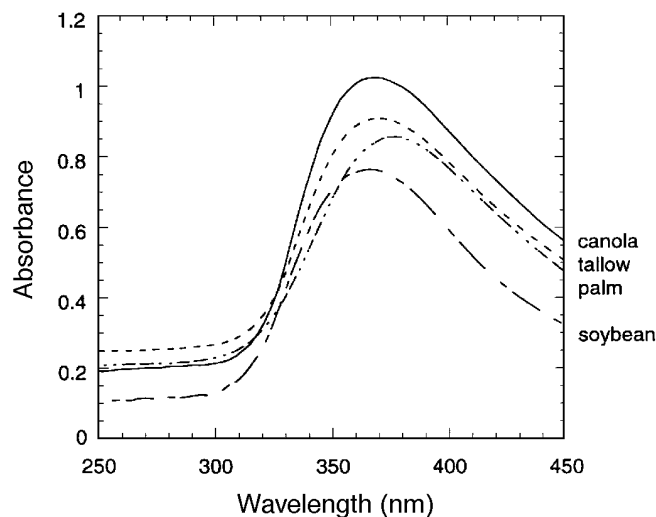
**Differential scanning calorimetry (DSC) and solid fat content (SFC).** Ten milligrams of oil samples were loaded on

stainless steel pans and then measured with a Perkin-Elmer DSC-7 (Norwalk, CT 06859). The programs of heating and cooling are listed in Table 2. The melting curves of these products from -30 to 70°C were used to calculate the SFC.

**High-performance liquid chromatography (LC).** Triglyceride profiles were analyzed under these conditions: Spherisorb C18 column, 15 cm × 4.6 mm, S3 OD2; Waters Alliance 2690 pump; ELSD IIA detector (Varex, MD). The mobile phase was a mixture of dichloromethane and acetonitrile at 0.7 mL/min. The initial ratio of dichloromethane and acetonitrile was 20:80 (vol/vol); it was changed to 30:70, 60:40, and 20:80 at 1, 30, and 31 min, respectively, after injection of samples. The peaks were identified by comparison with triglyceride standards and oils with known triglyceride compositions. The area percentage was used to quantitate the composition of triglycerides. The column temperature was 40°C.

**TABLE 2**  
Differential Scanning Calorimetry Programming Method

Temperature (°C)	Time (min)	Rate (°C/min)
30.0	0.0	50.0
75.0	1.0	20.0
-30.0	10.0	10.0
70.0	—	—



**FIG. 1.** All the oils tested—canola, soybean, palm, and tallow—gave the similar unique absorbance peak with the addition of sodium methoxide.

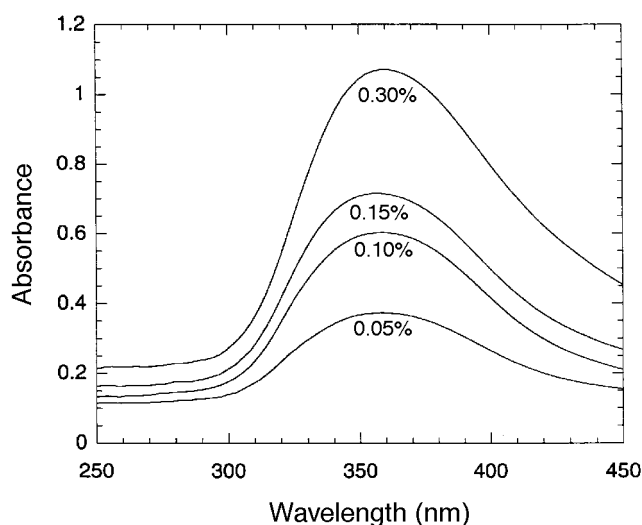


FIG. 2. The absorbance of oil mixture (canola oil/soy stearin, 70:30, w/w) increases with the addition of sodium methoxide (0.05–0.3%).

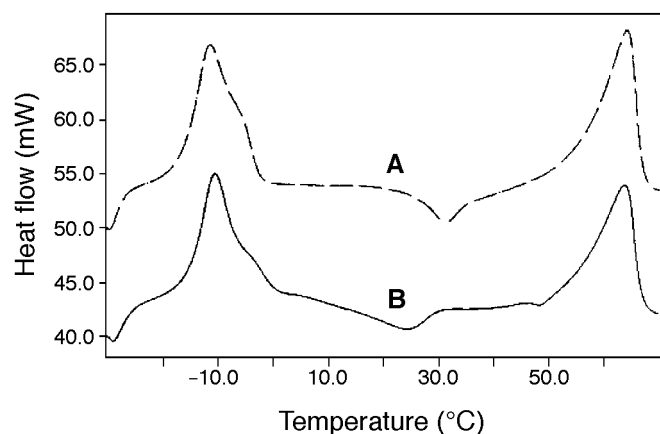


FIG. 3. The melting curve of the mixture of canola and soy stearin (70:30, w/w) started to change when the absorbance of 374 nm reached 0.4. (A) The physical blend without the addition of sodium methoxide; (B) the blend with addition of sodium methoxide and the absorbance of 374 nm is 0.4.

## RESULTS AND DISCUSSION

During interesterification, the oil changes color to a reddish brown after a chemical catalyst such as sodium methoxide is added. Color change is often used as an indicator for success-

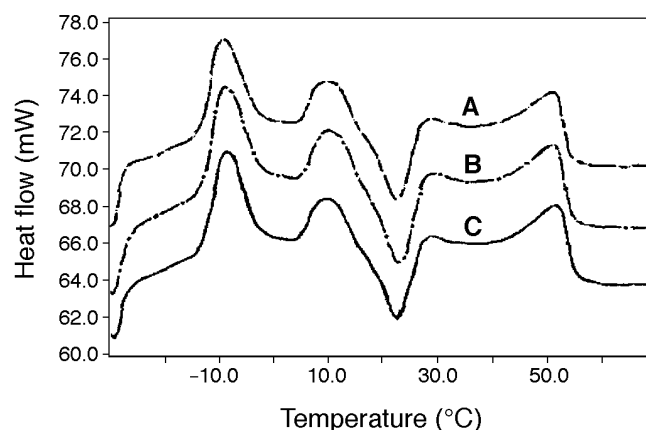


FIG. 4. The melting curve of the mixture of canola and soy stearin (50:50, w/w) interesterified at an absorbance of 0.8 stayed the same from 15 to 120 min at 120°C. (A) 15 min after the absorbance at 374 nm reached 0.8; (B) 60 min after the absorbance at 374 nm reached 0.8; (C) 120 min after the absorbance at 374 nm reached 0.8.

ful interesterification. This phenomenon has been known for a long time, but no spectrum has been reported. We found that absorbance by oil of visible and ultraviolet light increases after addition of sodium methoxide. One peak in particular appeared between 300 and 450 nm (the border between the ultraviolet and visible ranges) after the addition of a certain amount of sodium methoxide. This range represents the wavelength of blue color and therefore gives the oil a reddish brown color. Figure 1 shows the spectral peaks observed with canola-, palm-, soybean-, and tallow-based interesterifications. All the oils tested had the same unique peak regardless of their origin, fatty acid composition, unsaponifiable matter, and initial color. Therefore, the color substance is very likely involved in the mechanism of interesterification although its identity is still unknown.

The absorbance of oil increases as more sodium methoxide is added, as shown in Figure 2. The peak increases with the addition of more sodium methoxide. Figure 3 shows that the DSC melting curve of tested blends starts to change as the absorbance at 374 nm reaches 0.4. Below this critical absorbance, the melting curves did not change even when the reaction was run overnight. Interesterification equilibrated (randomized) when this absorbance reached 1.0 as shown by their SFC and triacylglycerol composition analysis (Table 3).

TABLE 3  
The Solid Fat Content and Triacylglycerol Composition of Canola/Soy Stearine (70:30, w/w) Before and After Interesterification

Absorbance	NaOMe (%)	Solid fat content (%) at temperature (°C)					Triacylglycerol composition										
		10.0	21.1	26.7	33.3	40.0	LOO	LOP	OOO	LOS	OOP	OOS	OPS	PPS	OSS	PSS	SSS
0.0	0.0	42	38	38	37	35	11.6	1.1	45.0	— <sup>a</sup>	3.7	1.6	—	—	—	6.8	24.1
1.0	0.3	47	25	22	15	9	5.3	2.4	17.8	6.9	6.0	33.3	4.5	0.7	15.0	1.1	2.0
1.1	0.4	47	25	22	15	9	6.2	2.7	19.9	7.1	5.2	31.7	4.6	0.8	13.8	1.1	2.0
1.3	0.5	47	25	22	15	9	5.7	3.0	16.6	7.8	5.0	32.9	4.9	0.9	13.9	1.0	1.4
Theoretical random calculation							5.5	1.0	21.8	5.3	5.8	31.4	5.6	0.2	15.0	1.3	2.4

<sup>a</sup>—, not detected; L, linoleic acid; O, oleic acid; P, palmitic acid; S, stearic acid.

**TABLE 4**  
The Solid Fat Content and Triacylglycerol Composition of Interesterified Canola/Soy Stearine<sup>a</sup> (70:30, w/w)

#	Absorbance	Solid fat content (%) at temperature (°C)					Triacylglycerol composition										
		10.0	21.1	26.7	33.3	40.0	LOO	LOP	OOO	LOS	OOP	OOS	OPS	PPS	OSS	PSS	SSS
1	0.00	42	38	38	37	35	11.6	1.1	45.0	— <sup>a</sup>	3.7	1.6	—	—	—	6.8	24.1
2	0.36	42	38	38	37	35	11.6	1.3	46.5	—	4.1	0.9	—	—	3.2	5.9	20.7
3	0.43	42	39	39	37	34	11.30	1.2	47.8	—	4.1	0.8	—	—	3.7	5.9	18.8
4	0.53	42	37	37	34	30	11.6	1.4	44.6	—	4.6	5.3	0.6	—	1.6	5.8	18.2
5	0.68	43	36	36	31	26	10.1	1.5	44.6	—	4.3	11.6	1.5	—	5.9	4.5	12.9
6	0.77	43	35	35	29	24	9.91	2.0	37.6	—	5.4	14.7	2.2	—	7.3	3.7	10.9
7	1.0	47	25	22	15	9	5.3	2.4	17.8	6.9	6.0	33.3	4.5	0.7	15.0	1.1	2.0

<sup>a</sup>For abbreviations see Table 3.

The same results are observed for the other blends of all the experimental oils listed in Table 1 (data not shown).

Interesterification was only partly achieved when the absorbance was between 0.4–1.0, and the degree of this partial interesterification depends on the absorbance. Figure 4 shows that the melting curves of partially interesterified test blends did not change up to 180 min at 120°C after the peak absorbance reached 0.8 with a reduced amount of sodium methoxide. Similar results were found when partial interesterification was conducted at various temperatures (data not shown). These results suggest that interesterification needs a minimum dosage of catalyst to initiate and complete (randomization) and the color compound is very likely the active catalyst.

A series of partial interesterifications was conducted by controlling absorbance. As shown in Table 4, partially interesterified oils (Samples 2–6) have solid fat contents and triglyceride compositions that depend on their degree of in-

teresterification, and these are different from both the physical mixture (Sample 1) and completely randomized product (Sample 7). By partial interesterification, the oil's physical properties such as melting point, SFC, and crystal form can be modified, providing an additional dimension to formulation options in product development. This method can give excellent repeatability as shown in Table 5.

This technology has also been applied to optimize the reaction conditions of randomization. Randomization has been widely used in industry to prepare functional products such as margarine oils and specialty shortenings. Because of the lack of on-line monitoring capability, randomization has been conducted with excess dosages of catalyst and varying reaction times. When processing conditions change, these conditions need to be readjusted. Therefore, excess time and/or catalyst are used to ensure complete randomization. This on-line monitoring system provides a novel way to monitor interesterification and significantly reduce reaction time and/or catalyst dosage, as demonstrated in our laboratory. With reduced catalyst and reaction time, the soap, the main byproduct in interesterification, will be reduced so the yield of product will be increased. Therefore, the cost of interesterification is significantly reduced and the capacity of interesterification can be increased without the expansion of processing equipment. Furthermore, the time for randomization is reduced to as short as 5 min by on-line monitoring technology, which is significantly shorter than the 15–30 min commonly used in conventional interesterification. With significantly reduced reaction time, on-line monitored interesterification produced

**TABLE 5**  
The Solid Fat Contents of Canola/Soy Stearine Mixtures (50:50, w/w) Interesterified at the Specific Absorbances

Absorbance	Solid fat content (%) at temperature (°C)		
	21.1	33.3	40.0
0.57	44	44	36
0.57	46	46	38
0.57	45	45	39
0.78	37	36	28
0.79	37	36	27
0.78	39	39	30

**TABLE 6**  
The Total Tocopherol Contents and Oxidative Stability of Interesterified Oils

Samples	Reaction conditions				RBD interesterified oils <sup>b</sup>	
	NaOMe (%)	Time (min)	Intesterification method	Degree of interesterification <sup>a</sup>	AOM (h)	Tocopherol (ppm)
Canola oil/soy stearin (50:50)	0.15	15	Conventional <sup>c</sup>	Randomized	27	100
	0.15	5	On-line monitoring <sup>d</sup>	Randomized	35	220
Soybean oil/soy stearin (50:50)	0.15	15	Conventional	Randomized	21	260
	0.20	5	On-line monitoring	Randomized	26	490

<sup>a</sup>Determined by differential scanning calorimetry melting curves.

<sup>b</sup>Refined, bleached, and deodorized (RBD).

<sup>c</sup>Conventional: the reaction was conducted at 95–100°C for 15 min after addition of sodium methoxide.

<sup>d</sup>On-line monitoring: the reaction was stopped once the absorbance at 374 nm reached 1.0; the reaction time was reported.

the products with higher oxidative stability and tocopherol content. Table 6 lists some of the results for the randomized products of canola and soybean oils with fully hydrogenated soybean oil. These data show that the total tocopherol contents are significantly higher (1.9–2.2 times) in on-line monitored interesterified products than that in the conventional interesterified ones. As a result, the former products have 5–8 h longer active oxygen method than the later ones.

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[Received September 21, 1998; accepted March 6, 1999]