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ORIGINAL PAPER

Low *trans*-Fat Spreads and Shortenings from a Catalyst-Switching Strategy

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Abstract Low *trans* fatty acid basestocks suitable for blending with liquid oils to make spreads and shortenings are prepared by using a two-step hydrogenation process. The first step uses a nickel catalyst to hydrogenate soybean, canola, high-oleic sunflower, and high-oleic safflower oils to a predetermined iodine value. At this point in the reaction, the second step commenced. Addition of a platinum catalyst at 80 °C and 73 psi hydrogen pressure allowed for hydrogenation to proceed to iodine values of 40–50. These products had 11–18% *trans* fatty acid content. These were then blended with soybean oil (5–50% basestock) to give products with bulk properties similar to commercial spreads and shortenings but with about one third the levels of trans fat.

Keywords Fats and oils · Hydrogenation · Processing Technology · Oleochemistry

Introduction

Prior to the First World War, margarines were prepared from lard and tallow due to their melting properties which are similar to butter, the expensive dairy product margarines were meant to replace. For a brief period, tropical oils like coconut and palm were extensively used owing to their melting properties and almost complete lack of flavor. Between the years 1922 and 1963 the use of animal fats and tropical oils used for margarine manufacture fell from 84% of total fats used to about 7% while, first, cottonseed, then soybean oil replaced these resources [1]. The successful use of soybean oil required stabilization of the liquid oil toward oxidation which causes the development of off flavors from rancidity. The source of the off flavors was the polyunsaturated linolenic acid. Hydrogenation of linolenic acid, which comprises about 8% of the fatty acid in soybean oil, was seen as the simple solution to the poor keeping properties of the oil. However, hydrogenation would cause loss of linoleic acid as well and this fatty acid was known to have beneficial effects in the diet. Therefore, the selective hydrogenation of linoleic acid became the goal of many research groups [2–5].

Partial hydrogenation of oils leads to the formation of both positional isomers caused by double bond migration from the 9-, 12-, and 15-positions, and geometric isomers formed as *cis* isomers become *trans*. Conditions which favor selective hydrogenation also favor formation of *trans* isomers [6]. Primarily this means high temperature and low hydrogen pressure lead to higher *trans* levels though catalysts also have an effect. In the triad of transition metals

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most frequently studied, platinum is most active and leads to lowest *trans* levels, palladium is selective but with low activity, and nickel is active with good selectivity [7]. Nickel, usually in the form of oxides mixed with alumina, is the most commonly used industrial catalyst. The incidental formation of *trans* fatty acids improves the bulk properties of the product: melting points and solid fat content are increased due to the high melting point of *trans* fats, and shortenings have greater plasticity [8, 9]. The drawback to having *trans* fats in foods is the correlation between *trans* fat consumption and increased risk of developing cardiovascular disease [10, 11]. Although this link has not always been certain [12], in January, 2006 the United States required nutrition labels to include the level of *trans* fat as part of the Nutrition Education Act of 1990. This has created an impetus to develop low, or zero-*trans* shortenings and spreads for the marketplace.

We have recently reported a hydrogenation method for the production of spreads and shortening oils that were low in *trans* fatty acid content [13]. That method, which utilized a common nickel catalyst for hydrogenation to low iodine values, yielded basestocks from soybean oil which were 32% *trans* fatty acid at IV 41 and 18% at IV 27. These were then blended with soybean oil to give products which had the physical properties, like dropping point and percent solid fat content, similar to those in commercial spreads and shortenings while having *trans* fatty acid content as low as 2%. Here we report that by using a catalyst switching strategy and other vegetable oils we can achieve very low levels of *trans* fatty acids in partially hydrogenated oils.

Materials and Methods

All oils were refined, bleached, and deodorized by the suppliers. Soybean, canola, and high oleic sunflower oils were from ADM (Decatur, IL, USA). The high oleic safflower oil was from PVO international (Hodgkins, IL, USA). All oils were stored at 0 °C prior to use. The nickel catalyst used was a commercially available catalyst (Nysosel 645) obtained from Englehard Corporation (Now BASF Catalysts, LLC), Erie, PA. It is composed of nickel oxide, nickel and alumina (25–40%) suspended in hydrogenated vegetable oil (60–75%). The platinum catalyst was 3 wt% Pt on carbon (Sigma-Aldrich, Milwaukee, WI, USA).

The hydrogenations were performed as previously described [14]. Reaction conditions for the nickel-catalyzed hydrogenations were 0.3 wt% Nysosel, 175 °C, 15 psi hydrogen pressure and moderate agitation. Reaction progress was monitored by refractive index taken at 70 °C. Once a target RI was reached, the bomb was purged with nitrogen and allowed to cool. The oil was then treated with 1.0 ml of an aqueous 50 wt% citric acid solution and 1.0 g tonsil bleaching earth (Sud-Chemie, Puebla, Mexico). The oil was then filtered through a pad of Celite.

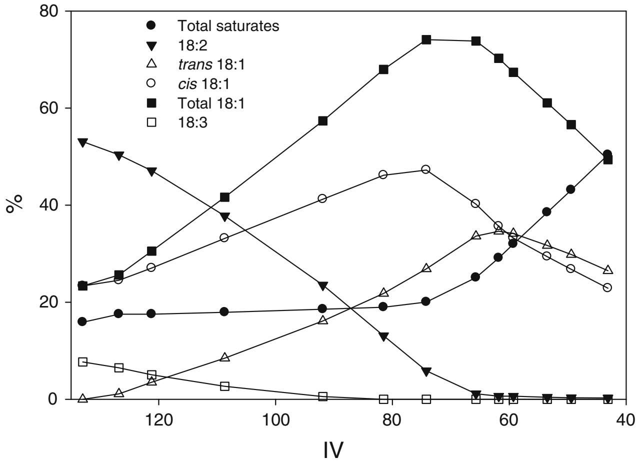

Fig. 1 Change in fatty acid profile of soybean oil during hydrogenation over the nickel catalyst Nysosel 645

The hydrogenations using the catalyst-switching strategy were performed as follows. The point at which the switch was made was chosen based on plots of fatty acid profile verses IV (see Figs. 1, 3, 5, 7) generated using Nysosel 645 as catalyst. Each of these shows a point at which the level of *trans* 18:1 begins to rise at an accelerated rate. It is at this point the reaction is stopped and the Nysosel catalyst removed. The platinum-catalyzed hydrogenations were carried out over 180 mg Pt/C per liter of oil, 80 °C, 73 psi hydrogen, with moderate stirring. The product was isolated as above. Fatty acid compositions were determined immediately after oil collection by gas

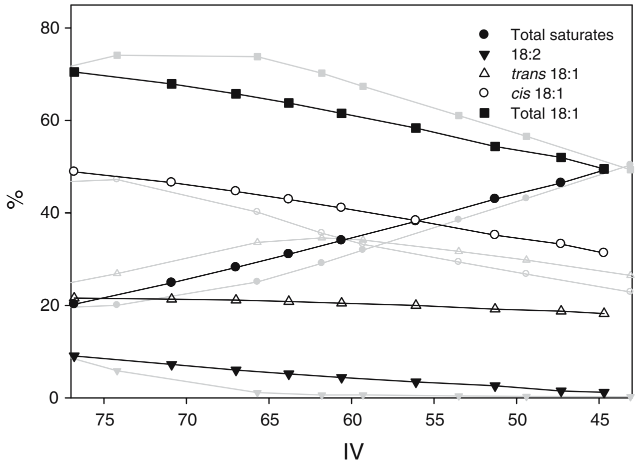

Fig. 2 Change in fatty acid profile of soybean oil after switching to the Pt/C catalyst after hydrogenation to IV 76 with Nysosel 645. Shown in *gray* is the profile from Fig. 1 which is produced when no catalyst switch is made

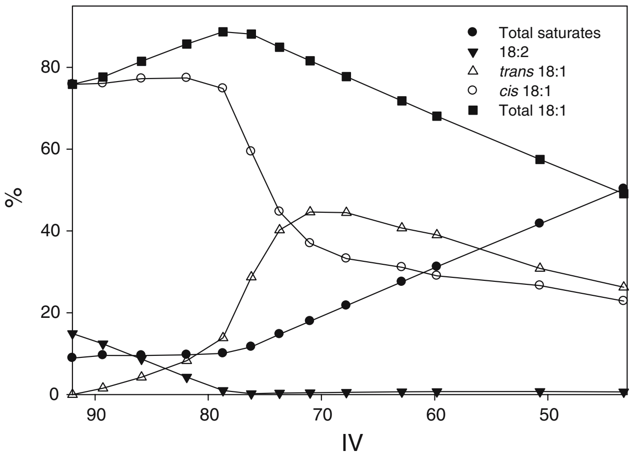

Fig. 3 Change in fatty acid profile of high-oleic safflower oil during hydrogenation over the nickel catalyst Nysosel 645

chromatography as described previously [15]. All hydrogenations were performed in duplicate.

Sample shortening blends were prepared by mixing liquid samples of the partially hydrogenated oils with soybean oil in ranges of 5–50 wt% basestock. These were used for dropping point and solid fat content analyses. Mettler drop melting point and solid fat content (nmr) were determined according to official AOCS methods [16].

Results and Discussion

Figure 1 shows the change in fatty acid profile of soybean oil as the IV is reduced from 133 to 41. (Although all reactions were run in duplicate, the figures show data of only a single experiment. The duplicate runs are omitted for clarity but the data were within 5% of those shown).

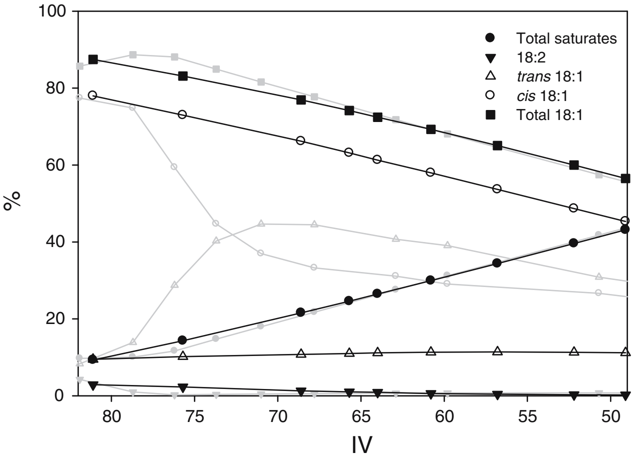

Fig. 4 Change in fatty acid profile of high-oleic safflower oil after switching to the Pt/C catalyst after hydrogenation to IV 81 with Nysosel 645. Shown in *gray* is the profile from Fig. 3 which is produced when no catalyst switch is made

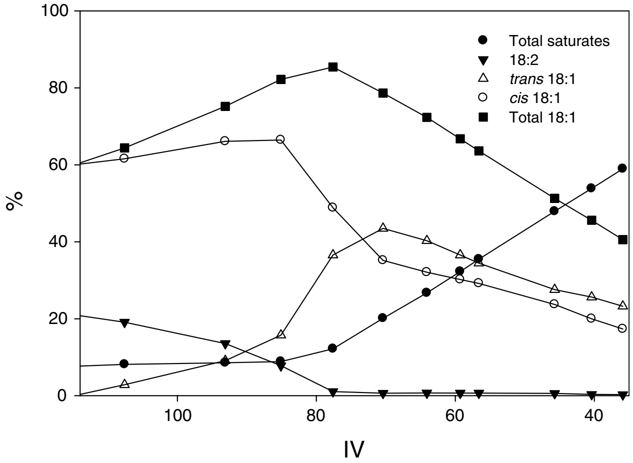

Fig. 5 Change in fatty acid profile of canola oil during hydrogenation over the nickel catalyst Nysosel 645

Notable from this plot is how the level of *trans* fatty acids continued to rise after the level of *cis* fatty acids had peaked. It is at the IV at which the *cis* fatty acids have peaked that the first stage hydrogenation was stopped and the catalyst was switched from the selective nickel catalyst to the nonselective platinum catalyst. Figure 2 shows the change in fatty acid profile of soybean oil starting at IV 76 after the catalyst switch. Although the Pt/C catalyst is considered nonselective toward polyunsaturated fats, it clearly reacts more rapidly with the *cis* 18:1 isomers than the *trans* isomers. This is evident from the slopes of the respective plots. The final oil was 19.8% *trans* fatty acids at IV 45, considerably lower than 26.5% *trans* found in the oil hydrogenated to IV 43 over Nysosel 645. It is the rapid reaction rate obtained from using platinum that makes the catalyst switch attractive. Although nickel catalysts are

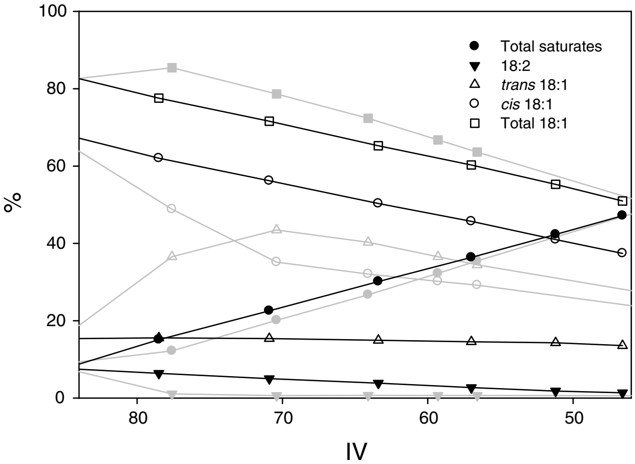

Fig. 6 Change in fatty acid profile of canola oil after switching to the Pt/C catalyst after hydrogenation to IV 84 with Nysosel 645. Shown in *gray* is the profile from Fig. 5 which is produced when no catalyst switch is made

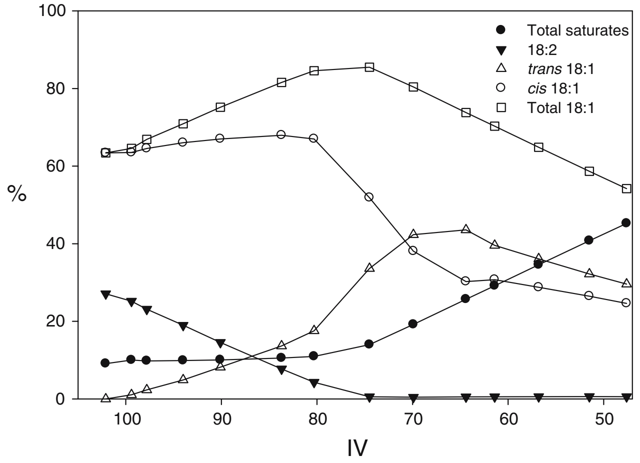

Fig. 7 Change in fatty acid profile of high-oleic sunflower oil during hydrogenation over the nickel catalyst Nysosel 645

active and will produce lower levels of trans fats at higher hydrogen pressure, the decreased throughput is not attractive to oil processors [14].

Figures 3 and 4 show the same data from the hydrogenation of high-oleic safflower oil. With an initial oleic acid composition of 76%, this oil showed a dramatic change in the relative concentrations of *cis*- and *trans*-18:1 as the IV falls from 82 to 74. When this isomerization was intercepted by switching catalysts at IV 81, a final product containing 14% *trans* fatty acids at IV 49 was obtained.

Figures 5 and 6 contain the data for the hydrogenation of canola oil with and without the catalyst switch, respectively. After exposure to the platinum catalyst starting at IV 84, this oil had a final *trans* level of 13.6% at IV 47. Figures 7 and 8 contain the data for the hydrogenation of high-oleic sunflower oil with and without the catalyst switch, respectively. After the addition of the platinum catalyst at IV 80, at a final IV of 47 this oil was 14% *trans* fat.

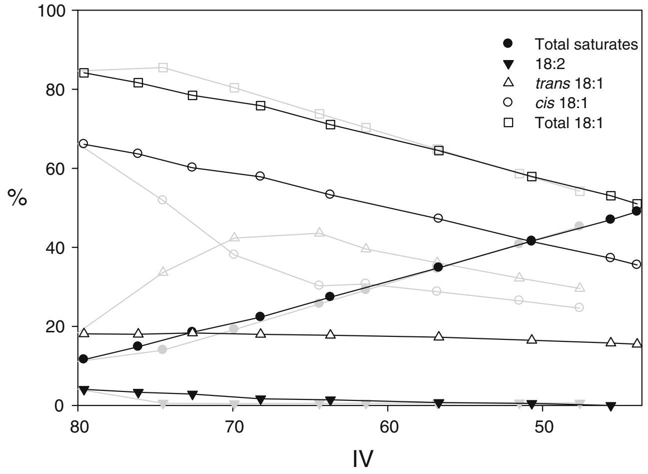

Fig. 8 Change in fatty acid profile of high-oleic sunflower oil after switching to the Pt/C catalyst after hydrogenation to IV 80 with Nysosel 645. Shown in gray is the profile from Fig. 7 which is produced when no catalyst switch is made

Table 1 Summary of the results showing the levels of *trans* fat in the hydrogenated oils using nickel or the catalyst-switching strategy

Oil	Catalyst or strategy[a]	Calc.% *trans* fat at IV 45[b]	*t*-test value
Soybean	Nickel	27.6 ± 0.4	0.0001**
	Nickel then Platinum	18.4 ± 0.1	
High-oleic safflower	Nickel	28.2 ± 1.3	0.0183*
	Nickel then Platinum	13.7 ± 2.9	
Canola	Nickel	28.0 ± 0.2	0.0001**
	Nickel then Platinum	14.0 ± 0.1	
High-oleic sunflower	Nickel	28.3 ± 0.9	0.0048**
	Nickel then Platinum	16.5 ± 0.7	

** Denotes significant differences between catalysts at $P \leq 0.01$; * Denotes significant differences between catalysts at $P \leq 0.05$

[a] The nickel hydrogenations were run using only this catalyst whereas the hydrogenations listed as "Nickel then Platinum" were started with nickel and then completed using platinum. See text for details

[b] % *trans* fat and standard deviation ($n = 2$) calculated from the line fitted to the data over the linear range

The statistical analyses of these results are summarized in Table 1. For comparison purposes, the data were fitted to a line over the IV range of about 40–65 and the *trans* fatty acid levels were calculated at IV 45. It is over this IV range that the oils show linear changes in the *trans* fat level. Results from the *t*-test indicate that the *trans* fat levels in the hydrogenated oils prepared using the two strategies are statistically different.

Table 2 lists the initial fatty acid content of the oils under study and Table 3 the physical properties of the hydrogenated oils and selected blends of these oils with soybean oil. As can be seen in Table 3 blends of very low levels of *trans* fatty acids can be prepared which have properties similar to commercial shortenings. All-purpose

Table 2 Percent fatty acid content of the oils studied

Fatty Acid	Seed Oil			
	Soybean	Canola	High-oleic safflower	High-oleic sunflower
16:0	10.6	4.5	5.6	4.3
18:0	4.5	2.0	2.4	3.6
18:1 *trans*	0.0	0.2	0.0	0.0
18:1 *cis*	23.3	59.4	75.8	63.4
18:2	53.1	20.8	14.9	27.1
18:3	7.7	10.9	0.3	0.2
20:3	0.4	0.7	0.5	0.3
20:1	0.0	1.3	0.0	0.2
22:0	0.4	0.4	0.4	0.9

shortenings have dropping points between 42 and 48 °C and solid fat contents of 3–9% at 40 °C and have 12–25% *trans* fatty acid content. Each basestock has at least one soybean oil blend falling into this dropping point and SFC range with much lower levels of *trans* fat. For example, the 15% canola blend has a dropping point of 45.5 °C and is 4.2% solids at 40 °C while containing only 2.0% *trans* fat.

A blend that has properties similar to commercial spreads results from a 5% canola basestock in soybean oil. Spreads have dropping points of 31–32 °C and solid fat content of 1–2% at 33.3 °C. The 5% canola falls into these ranges and is only 0.7% *trans* fatty acids compared to 10–13% commercial products. However, commercial spreads have completely melted at 40 °C but the canola blend is still 0.2% solids at 45 °C and completely melted only at 50 °C. Although this does not necessarily mean this blend would produce a satisfactory spread, results like these can be used to select basestocks for scaled up production and eventual blending for spreads or crystallization for shortenings.

We have shown that a simple catalyst-switching strategy can be used to produce basestocks of very low *trans* fatty acid levels. These can be blended to give products with physical properties similar to commercial shortenings and

Table 3 Physical characteristics of basestocks prepared using the two-step hydrogenation and blends made with soybean oil

Basestock	Percentage of basestock[a]	% *trans*	Dropping point	SFC[b]										
				0 °C	10 °C	21.1 °C	26.7 °C	33.3 °C	40 °C	45 °C	50 °C	55 °C	60 °C	65 °C
Canola oil														
IV 46	100% basestock	13.1	63.8	63.6	57.9	51.3	50.6	47.5	39.5	32.6	26.9	18.7	11.1	0
	5% basestock	0.7	30.9	2.9	2.6	1.9	2.1	1.4	1.2	0.2	0	0	0	0
	10% basestock	1.3	39.3	5.2	4.7	3.8	4.3	3	2.5	1.3	0.8	0	0	0
	15% basestock	2.0	45.5	7.7	6.5	6.5	6.5	6.2	4.2	2.7	1.6	0	0	0
	20% basestock	2.6	48.7	10.7	10	8.1	8.2	7.9	5.8	4.6	2.6	0	0	0
	25% basestock	3.3	51.1	14.3	12.7	10.9	10.7	10	7.5	5.6	4.2	1.1	0	0
	50% basestock	6.6	57.5	30.1	26.6	23.2	23.1	20.1	17.7	14.5	10.4	5.7	0	0
Hi-oleic safflower oil														
IV 49	100% basestock	11.2	61.9	53	50.1	43.9	43.5	40	33.1	26.7	21.7	14.4	4.7	0
	5% basestock	0.6	36.8	2	2.4	2	1.6	1.2	0.6	0.6	0	0	0	0
	10% basestock	1.1	37.8	4.9	4.2	3.6	3	3	2	1.1	0.7	0	0	0
	15% basestock	1.7	42.9	6.7	6.2	5.4	4.7	4.2	2.9	1.8	1.1	0.2	0	0
	20% basestock	2.2	46.9	9	9.2	7.3	7.6	6.3	4.2	3.4	2.3	0.5	0	0
	25% basestock	2.8	51.3	13.2	12	9.5	9.2	8.3	6.6	4.3	3.3	0.6	0	0
	50% basestock	5.6	56.0	27.3	23.6	20.3	19.8	18.1	13.9	11.3	8.8	4.8	0.4	0
Hi-oleic sunflower oil														
IV 44	100% basestock	15.5	62.7	70.7	64.5	58.5	58.2	53.9	44.6	37.5	31.1	20.4	9.3	0.1
	5% basestock	0.8	42.2	3.6	3	2.8	2.7	2.2	1.3	0.9	0.6	0	0	0
	10% basestock	1.6	46.1	5.5	5	4.3	4.4	4	2.7	1.5	1	0	0	0
	15% basestock	2.3	47.6	9.1	8.1	7.2	6.5	5.7	4.1	3.4	2.4	0	0	0
	20% basestock	3.1	49.9	14.2	11.7	10.1	10.1	9.1	6.9	4.7	3.7	0.4	0	0
	25% basestock	3.9	52.0	16.9	14.8	12.8	12.1	11.3	8.1	6.1	49	0.7	0	0
	50% basestock	7.8	58.0	34.1	30.2	26.5	26.3	23.5	19.1	16	12.3	6.8	0.1	0
Soybean oil														
IV 45	100% basestock	18.2	60.0	81	76.6	58.9	52	47.8	40.5	31.2	22.3	13.4	1.4	0.4
	5% basestock	0.9	29.3	3	2.9	1.9	2.3	1.5	1.2	0.5	0	0	0	0
	10% basestock	1.8	38.8	7.5	6.3	4.5	4	3.4	2.2	1	0.1	0	0	0
	15% basestock	2.7	44.5	12.2	9.6	7	6.4	6.8	2.4	2.2	0.6	0.5	0.5	0
	20% basestock	3.6	47.7	16	12.6	10.2	9.4	8.3	5.7	3.4	1.7	0.4	0.3	0
	25% basestock	4.6	49.3	18.4	15.8	11.9	11	9.3	6.6	4.3	2.5	0.6	0.2	0
	50% basestock	9.1	55.1	26.3	32.7	26.4	24.2	21.7	17.1	11.6	7.5	3.6	0	0

[a] Balance soybean oil

[b] Solid fat content by pulsed NMR

spreads and lower in *trans* fatty acid levels. These properties could be further refined by substituting other vegetable oils for the soybean oil used here or by the addition of tristearin to the blends. A small amount of tristearin could be added to increase the solids content and dropping points without the addition of *trans* fatty acids.

The method described here could easily be performed in existing commercial equipment using readily available catalysts. We isolated our first-stage, partially hydrogenated product after hydrogenation over nickel prior to hydrogenation over platinum. This makes the process appear more cumbersome than it need be. Since the Nysosel 645 is inactive at 80 °C, the reaction would only need to be cooled to this temperature and the platinum catalyst added and the hydrogen pressure increased to 73 psi for the second stage to commence. The two catalysts could then be removed in a single filtration.

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