

# Partial Hydrogenation and Winterization of Soybean Oil<sup>1</sup>

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## Abstract

Soybean oil was hydrogenated under selective and nonselective conditions to give products with iodine values (I.V.) ranging from 85–115. The products were crystallized at 8C and examined for yield, stability, and fatty acid composition of the winterized oil. Changes in fatty acid composition, formation of *trans* acids, and yield of winterized oil are approximately linear with the degree of hydrogenation. Stearine fractions, which are 15–20 I.V. units lower than winterized oil, were further crystallized in solvents to yield liquid oils and hard stearines.

## Introduction

PARTIAL HYDROGENATION of soybean oil was patented by Durkee (4) in 1944 as a means of obtaining improved flavor stability. Since then many patents and publications related to hydrogenation and flavor improvements of soybean and other vegetable oils have appeared (1,6,7,10,17–18,20,22). Traditionally, about 85% of the soybean oil going into edible products has been hydrogenated. Uses of the liquid oil have been largely limited to areas where the oil is not exposed to high temp or to prolonged storage under adverse conditions. In 1960, retail markets offered a partially hydrogenated, winterized liquid soybean oil with improved stability characteristics. This general-purpose salad and cooking oil was obtained through a marked reduction in the linolenic acid content along with some lowering of the I.V.

The dietary quality and chemical analysis of one such oil were reported by McOsker et al. in 1962 (13) in a biological study on the serum cholesterol levels developed by several different fats. Chemical analyses of shortening and of winterized oils were made by Jones et al. (9) to determine the natural fatty acids and fatty acid isomers formed during hydrogenation.

Oils low in linolenic acid were obtained through the winterization and fractionation of soybean oil hydrogenated to I.V. between 85 and 110. The characterization and yields of these oils are reported in this study.

## Materials and Methods

**Soybean Oil.** A single lot of commercially refined and bleached soybean oil (I.V. 128, linolenic acid 6.8%) was used throughout the investigation.

**Catalysts.** Nickel hydrogenation catalysts of the type generally used industrially as a fully selective catalyst functioning over a wide range of conditions were obtained from two commercial sources. Catalyst A contained 24.4% nickel; catalyst B, 25.5%; both were protected in hardened oil and reportedly could be stored indefinitely without loss of activity.

**Hydrogenation.** One-gallon samples were hydrogenated in a 3-gal stainless-steel convertor equipped with a special mixing stirrer (3) in the pilot plant of the Northern Laboratory. Hydrogen uptake was measured by a differential manometer, which was used to indicate the desired degree of conversion. To

avoid possible side effects of hydrogenation, samples were not taken during a run. Conditions for selective hydrogenation were 170C and 5-lb hydrogen pressure; generally, a catalyst concentration of 0.2% nickel was employed. Nonselective conditions were 120C and 100 lb pressure with the same amount of catalyst. Stirring was conducted at 1,380 rpm, which violently agitated the oil.

**Winterization.** The hydrogenated samples were slowly cooled in 1-gal wide-mouthed Dewar flasks in a 46F (8C) constant temp room. After standing for at least 4 days, the winterized oils were filtered without suction through coarse cloth in large Buchner funnels. The stearine cake was compacted by placing a rubber dam over the funnel and applying suction, provided by a laboratory vacuum pump. Pressing yielded from 5–20% more liquid than did gravity filtration.

**Gas Chromatography.** All fatty acid compositions were determined on distilled methyl esters prepared through transesterification with a sodium methoxide catalyst. A Beckman instrument, model GC-2A, equipped with a disc integrator and fitted with a 10% diethylene glycol succinate (DEGS) 6 ft × ¼ in. column, was used in analyzing the hydrogenated stocks. An Aerograph dual column, model 330A, fitted with 6 ft × ¼ in. columns 25% DEGS, was used to analyze acetone-fractionated samples.

**Fractionation.** Three liters of a 20% (w/w) solution of the stearines in acetone were allowed to cool slowly to ambient temp in 1-gal Dewar flasks in an 8C cold room. When 2 liters of the filtrate from the 8C crystallization were further cooled in a 16C cold room, a liquid and a stearine fraction were obtained after equilibrating at this temp.

**Melting Point.** The melting points were determined by the AOCS capillary tube method Cc 1-25 (16).

**Trans Acids.** *Trans* acids were determined by the method of Shreve, Heether, Knight, and Swern (19).

**Organoleptic Evaluation.** Flavor scores for deodorized oils were obtained by panel testing as described in a previous publication (15).

## Results

Published hydrogenation curves for soybean oil indicate that I.V. of 90 or lower must be attained to remove linolenic acid. Figures 1 and 2 show the compositions of soybean oils hydrogenated under selective and nonselective conditions to the extent that the linolenic acid content has been reduced to less than 3%. Because results were almost identical in evaluating the nickel catalyst from different commercial sources, the two runs can be considered replicates. Both catalysts proved highly selective under the conditions used as the stearic acid content did not show an increase even when the oils were hardened to I.V. below 90. *Trans* acid formation was similar in the selective series of runs and showed a consistent ratio of 0.73 for *trans* acid per unit iodine drop. Under these conditions *trans* bond formation is a direct linear function of the amount of hydrogenation. This linearity should hold until the I.V. drops to the area where *trans* bonds are hydrogenated, which is reported to be at I.V. of 70–80 (22).

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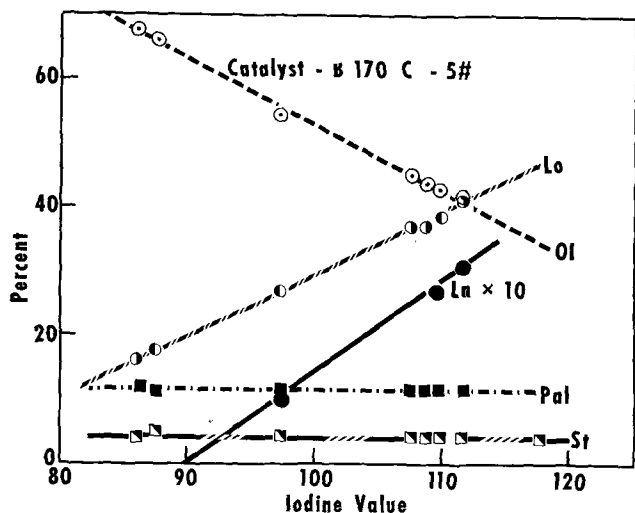


FIG. 1. Relationship between fatty acid composition of selectively hydrogenated soybean oil and the I.V. (Pal, palmitic; St, stearic; Ol, oleic; Lo, linoleic; Ln, linolenic.)

Fatty acid compositional changes are plotted as straight-line functions over this limited range of I.V. This choice was for clarity although it is realized that the linear relationship does not hold at lower I.V. Within the limits of accuracy of analytical methods (duplicates better than 0.5%), the increase in oleic (monounsaturated) acid content is equal to the sum of the loss of linoleic and linolenic.

Figure 2 illustrates a nonselective hydrogenation with the same catalysts as employed under the selective conditions (Fig. 1). Nonselective conditions are not as satisfactory as selective conditions for preparing winterized oil since stearic acid content has increased and since linolenic acid content has not been reduced to levels attainable under selective conditions. However, if a low *trans* acid content is the most important criteria for the finished oil, then nonselective conditions should be employed. Figure 3 shows the rate of cooling of an oil, hydrogenated to an I.V. of 87.5, which started to crystallize when the temp reached 25°C. Crystallization of the major amount of the stearine took place during the next 25 hr, after which the amount deposited was too small to be detected by thermal measurements. Unhydrogenated soybean oil formed no crystals under these

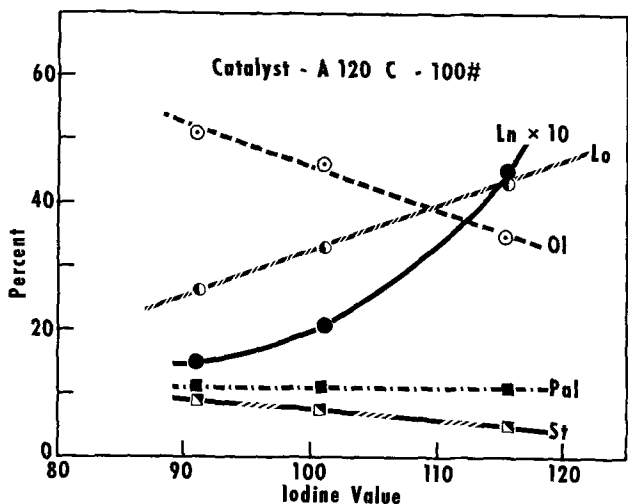


FIG. 2. Relationship between fatty acid composition of non-selectively hydrogenated soybean oil and the I.V.

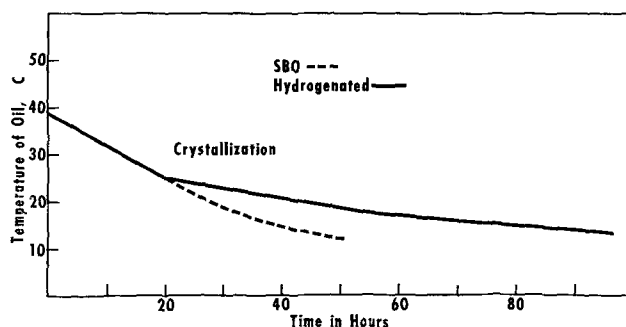


FIG. 3. Winterization cooling curve of soybean oil (SBO) and soybean oil hydrogenated to an I.V. of 87.5.

conditions. Winterization cooling curves were obtained by a thermocouple positioned in the center of the Dewar flask, and the temp change was followed on a strip chart recorder.

Yields of winterized oil ranging from 60 to over 90% and their *trans* acid contents are shown in Figure 4. Yield data are plotted against the I.V. of the winterized oils. I.V. for the winterized oils were 3-10 units higher than for the hydrogenated oil from which they were obtained. Considerably lower yields of oil are indicated from nonselectively hydrogenated stocks. The latter oils are, in general, higher in linolenic, linoleic, and stearic acids as well as lower in *trans* acid content.

Separate curves are shown for the yield of winterized oils obtained from the runs made with two different selective catalysts. However, the scatter of points is probably due to errors and difficulties encountered in the winterization step, and all points irrespective of the catalyst used could be represented by a single line. The marked decrease in oil yield at I.V. below 100 can probably be attributed more to

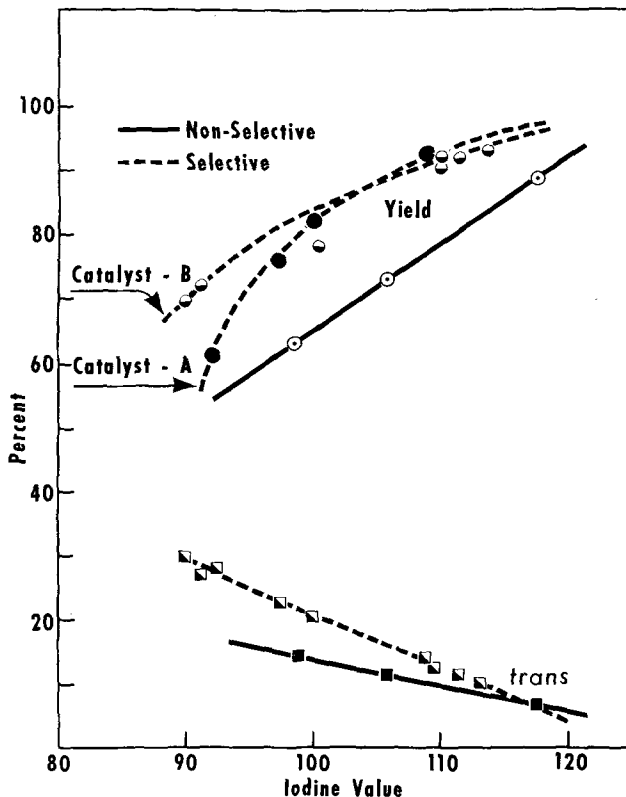


FIG. 4. Yield of winterized oil in relation to *trans* acid content and I.V.

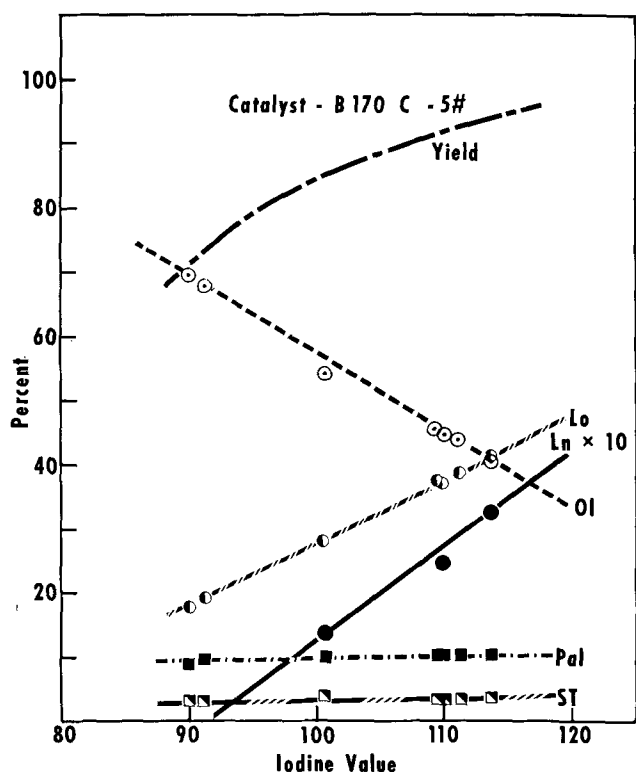


FIG. 5. Relationship between fatty acid composition of selectively hydrogenated-winterized oil and I.V.

the liquid oil retained by the stearine cake than to the increased content of saturated and *trans* acids. Duplication of yield data in this area has been difficult, and the problem has been attributed to unknown factors affecting the course of crystallization. Processing difficulties and low yields indicate that oils hydrogenated to I.V. of approximately 90 would have to be winterized and handled in a solvent system.

Composition of each winterized oil obtained from selective hydrogenations is shown in Figure 5. The palmitic and stearic acid contents do not vary appreciably with the I.V. of the winterized oil, and all saturated acid values are slightly lower than those for the original soybean oil. Linolenic acid is found in all winterized oils having an I.V. above 90. Winterized oils having 1 and 2% linolenic acid contents will have I.V. of approximately 99 and 105, respectively. At levels of 3% linolenic acid, winterized oils with I.V. of approximately 110 can be obtained in yields of 90%. When levels of 3% linolenic acid are attained, the linoleic acid is reduced to 40% from its initial level of 50%, but when hydrogenation is continued to remove all the linolenic acid, the linoleic acid level drops to approximately 20%.

Figure 6 shows the relationship of the *trans* acid content of selectively hydrogenated oil to that of its winterized fractions. The difference in I.V. of the respective fractions for each level of hydrogenation is also apparent from this graph.

Unsatisfactory yields of winterized oil low in linolenic acid suggested experiments on solvent fractionation. Acetone was selected because of its ability not only to separate saturated from monounsaturated glycerides but also to separate these from the higher unsaturated ones (8,14,21).

Fractionation of the stearines, (Fig. 7) at temp of 6C and -16C produced a large amount of liquid oil. Fatty acid analyses (Table I) indicated that the

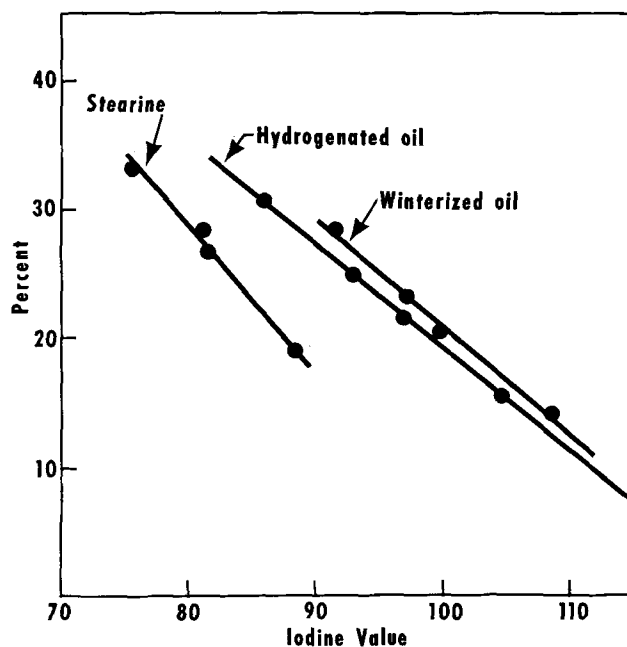


FIG. 6. Relationship between I.V. and *trans* acid content of selectively hydrogenated soybean oil and its winterized fractions.

soluble fractions will vary widely in composition depending on the temp of fractionation. Composition of the fractions soluble at 6C is approximately equivalent to that of the winterized oil, however, the melting point of the fraction from selective hydrogenation is too high, 17C, for a salad oil. Further fractionations conducted at -16C gave greatly reduced yields but oils of very low melting points, below -16C. The optimum fractionation temp is probably near 0C.

The fractionated stearines were analyzed by the lipase hydrolysis technique (5,12) to determine if any selective fractionation could be demonstrated. A study of the distribution of linoleic acid in the  $\beta$ -position of both the winterized and the solvent-fractionated oils indicates that for selectively hydrogenated soybean oil, there has been some selection favoring the 2-linoleyl glycerides. Since hydrogenation has been shown to be nonselective for glyceryl

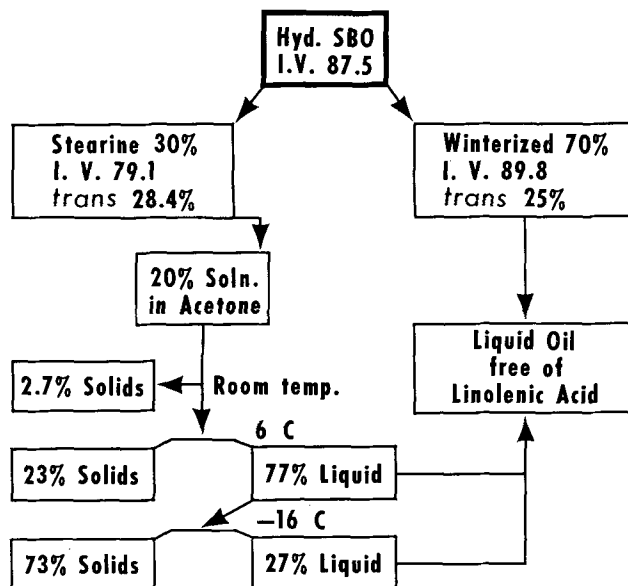


FIG. 7. Winterization and solvent-fractionation flow sheet of selectively hydrogenated soybean oil.

TABLE I  
 Fatty Acid Composition of Hydrogenated and Fractionated Soybean Oil

Sample	Composition of fractions								
	I.V.	Yield %	M.P., C	Trans, %	Pal <sup>a</sup> %	Stearic %	Oleic %	Lo <sup>a</sup> %	Ln <sup>a</sup> %
Soybean oil.....	126.7	.....	.....	Tr	11.8	4.2	26.9	50.2	6.8
Hydrogenated (selective).....	87.5	.....	.....	25.5	10.9	4.9	66.5	17.7	Tr
Winterized.....	89.8	69.7	8	25.1	9.6	3.0	68.2	19.2	Tr
Stearine.....	79.1	30.3	39	28.4	14.1	8.0	63.2	14.7	Tr
Acetone fractions.....									
6C Liquid.....	87.2	77.0	17	25.7	11.9	3.9	67.2	16.9	.....
-16C Liquid.....	94.4	27.0	<-16	19.3	7.0	1.6	73.3	17.4	.....
-16C Solids.....	80.6	73.0	19	28.8	13.6	6.1	67.1	12.9	.....
6C Solids.....	46.3	23.0	49	34.4	26.1	23.0	47.5	3.0	.....
Hydrogenated (nonsel.).....	90.9	.....	.....	16.1	11.6	9.4	51.4	26.1	1.5
Winterized.....	98.5	63.2	7	14.0	10.1	8.4	50.7	29.1	1.7
Stearine.....	78.0	36.8	51	18.8	13.4	11.3	53.4	21.0	0.9
Acetone fractions.....									
6C Liquid.....	97.0	70.4	10	18.1	11.1	8.0	51.6	27.2	2.1
-16C Liquid.....	11.5	33.0	<-16	15.0	7.3	3.9	50.2	36.7	1.8
-16C Solids.....	87.4	67.0	16	18.2	13.4	11.4	50.1	24.2	0.9
6C Solids.....	32.2	29.6	56	20.7	18.3	47.0	31.9	2.8	.....

<sup>a</sup> Pal, palmitic; Lo, linoleic; Ln, linolenic.

position (11), an increase of the percentage of linoleic acid in the  $\beta$ -position can be explained on solvent selectivity. The percentage of linoleic acid in the  $\beta$ -position increased from 46.5% in natural soybean oil, to 56.9% in winterized oil, and to 60.7% in the liquid fraction of the -16C solvent-fractionated stearine. No difference could be shown in the distribution of linoleic acid in the  $\beta$ -position in any of the fractionated samples obtained from nonselectively hydrogenated soybean oil.

Over 90% of the linoleic acid is removed from the winterized stearine fraction by solvent crystallization from acetone at 6C (Table I). Solvent selectivity that favors linoleic acid and the 2-linoleyl glycerides is important nutritionally. Except for the small amount of isomers derived from linolenic acid reduction it may be assumed that most of the linoleic acid in the  $\beta$ -position of the winterized oil is the unaltered natural *cis,cis* linoleic acid. Solid fats melting much above 40C cannot be analyzed by the lipase method because of temp limitations of the enzyme. Thus, it was not possible to obtain structural data on the hard stearine fractions. Further studies are being undertaken to establish the significance of these observations.

The very low linoleic acid content, from 1-3%, in all the acetone insoluble fractions indicates this solvent is suitable for fractionating partially hydrogenated soybean oil. Although data are limited, all results warrant more extensive studies since the physical properties of acetone also make it an economical solvent to evaporate and recover.

Table II shows the stability of the winterized oils

TABLE II

Organoleptic and Oxidative Stability Evaluation of Hydrogenated-Winterized Soybean Oil

Sample	I.V.	% Ln <sup>a</sup>	Flavor		AOM -P.V. <sup>b</sup> 8 Hr -98.6
			Initial	4 days -60	
With 0.01% Citric Acid					
Control.....	127	6.8	7.6	7.0	5.0
Winterized.....	111	2.2	7.8	6.8	2.4
Winterized.....	101	1.4	7.8	6.7	2.0
Winterized.....	91	Tr	6.9	6.9	1.5
Without Citric Acid					
Control.....	127	6.8	8.3	5.9	18.5
Winterized.....	111	2.2	6.1	4.5	36.0
Winterized.....	101	1.4	6.8	5.2	24.0
Winterized.....	91	Tr	6.5	4.6	15.7
Samples					
Commercial A.....	110.6	2.9	7.3	6.2	2.9
Commercial B.....	114.2	2.3	8.3	7.1	2.6
Commercial C.....	113.3	3.0	8.0	6.7	1.9
Commercial D.....	108.5	2.0	7.0	6.5	12.4

<sup>a</sup> Ln, linolenic; Tr, trace.

<sup>b</sup> Peroxides developed after 8 hr under AOM conditions.

as measured by organoleptic evaluations and by oxidative tests. The initial flavor of the oils, when deodorized (3 hr-210C) with citric acid, does not show any relationship to either the I.V. or the linolenic acid content. Oxidative stability varies directly with I.V. in either the citric acid-protected or unprotected oils. Flavor scores of all samples are approximately equal and high. The control soybean oil used in these experiments proved more stable than an average soybean oil. Rigorous laboratory deodorizations are required because of difficulty in removing the typical hydrogenation flavor and odor. The need for metal inactivation in shown even for those oils of lower I.V. by a comparison of the noncitricated oils against the citricated samples. Removal of residual catalyst and trace metals cannot be overstressed in unsaturated fats processed with metal catalysts.

## ACKNOWLEDGMENT

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