Hydrogenation of Soybean Oil With Commercial Copper-Chromite and Nickel Catalysts: Winterization of Low-Linolenate Oils[1]

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ABSTRACT

Soybean oil hydrogenated in the presence of copper-chromite catalysts to 3% linolenate and below requires winterization if it is to pass the cold test. Yields of winterized oil from soybean oil hydrogenated to several linolenate levels were therefore studied. Partially hydrogenated soybean oil was sampled and filtered at intervals during hydrogenation on a pilot plant scale with a commercial copper-chromite catalyst. Samples were then vacuum bleached and filtered to remove dissolved copper, held at 7 C for 48 hr and filtered to remove stearines. The filtered winter oils passed the standard 5.5 hr cold test. For soybean oil in which linolenate was reduced to 0.1% with a commercial copper-chromite catalyst or to 3.0% with a nickel catalyst yields of winter oil were about the same; 92% for a 5.5 hr cold test oil (winterized two days at 7 C) and 89% for a 20 hr cold test oil (winterized two days at 4 C).

INTRODUCTION

The major factor responsible for the relative instability of soybean oil for food uses is widely recognized as the linolenate present in the oil (1-5). Attempts to eliminate this fatty acid from soybean triglycerides by selective plant breeding have not been successful (6). Partial hydrogenation of soybean oil, with the use of nickel catalysts, followed by low temperature winterization and separation of a stearine fraction, is now generally practiced industrially to produce a salad oil of lowered linolenate content. But products being marketed still contain several per cent of linolenate.

Koritala and Dutton (7-9) at the Northern Laboratory, as well as workers abroad (10-13), have reported selective hydrogenation of the linolenate in soybean oil by the use of copper-containing catalysts. Others (14-19) have combined copper with nickel or used nickel and copper catalysts in a two-stage independent hydrogenation of soybean oil to improve selectivity. We have previously shown in pilot plant tests (20) that several commercial copper-chromite-type catalysts, prepared correctly, are active and selective for this purpose. However, when selective hydrogenation of soybean oil with these catalysts is continued to a linolenate content below 3%, the oil does not meet the standard cold-test specifications for a salad oil, although such an oil may be satisfactory as an ingredient in mayonnaise (21).

For many years a salad oil has been produced through the winterization of cottonseed oil (5,22-26). The yield of a winterized cottonseed oil has been improved by the use of crystal inhibitors (23,26,27) and the winterization process has been hastened by the incorporation of solvents (28). Partially hydrogenated soybean oil, with the hydrogenation catalyzed by nickel, has been successfully winterized with and without solvents or crystal inhibitors (1,4,5, 11,13,15,19,21,19). Okkerse et al. (13) reported comparative winter oil yields for soybean oil hydrogenated with copper-chromite and nickel catalysts. They stated that the increase in fluidity of a "copper-hardened" soybean oil was due to the high selectivity of the catalyst which, in turn, produced a higher winter oil yield. Weiss (26) found that a less viscous oil improved winter oil yield because of increased "mobility."

Toyama (19) observed that the precursor to soybean oil's hardening flavor and components, which adversely affected the oil's stability, concentrated in the stearine fraction.

The present investigation was conducted to determine the yields of winter oil from soybean oil hydrogenated with commerical copper-chromite catalyst for various linolenate levels and to compare these yields with those of partially hydrogenated soybean oils when nickel was the catalyst.

EXPERIMENTAL PROCEDURES

Soybean Oil

A single drum of commercially refined and bleached soybean oil was used for comparative hydrogenation-winterization studies.

Catalysts

The copper-chromium-barium catalysts were two commercially prepared ones that had been found in previous tests to be highly active for hydrogenating soybean oil (20). A commercially reduced nickel catalyst (25% Ni in hardened oil), like those conventionally used to hydrogenate soybean oil, provided comparative data.

Hydrogenation

Thirty-five pounds of refined and bleached soybean oil was partially hydrogenated in a 10 gal autoclave (Autoclave Engineers, Inc.) equipped with a variable speed, magnetically driven, gas dispersion agitator (1400 rpm). The two commercial copper-chromite catalysts were compared under similar hydrogenation conditions, i.e., 1% or 0.5% catalyst, reaction temperature of 170 C and hydrogen pressure of 30 psig. The oil hydrogenated to an IV of 114 in 27 min when 1% catalyst was used. Nickel (25% in hardened vegetable oil) was used at a catalyst concentration of 0.2% (Ni concentration of 0.05%), a reaction temperature of 150 C, and 5 psig. Hydrogenation time to IV 114 with nickel catalyst was nearly the same as with 1% copper-chromite catalyst. The catalyst was added to the cold oil; the autoclave purged with N_2 and evacuated; the oil catalyst heated to the reaction temperature under 26 in. vacuum, purged with H_2 and placed under H_2.

Quart samples were taken periodically from the convertor, rapidly cooled under carbon dioxide to protect from oxidation, and filtered through filter aid in a Buchner funnel. After hydrogenation, the convertor was evacuated, the remaining oil cooled to 80 C under vacuum and the remaining portion of the batch filtered.

Bleaching

Each sample was vacuum-bleached with 2% acid-activated bleaching earth at 110-120 C for 15 min, cooled to 70 C and filtered to reduce the amount of metals dissolved in the hydrogenated oil.

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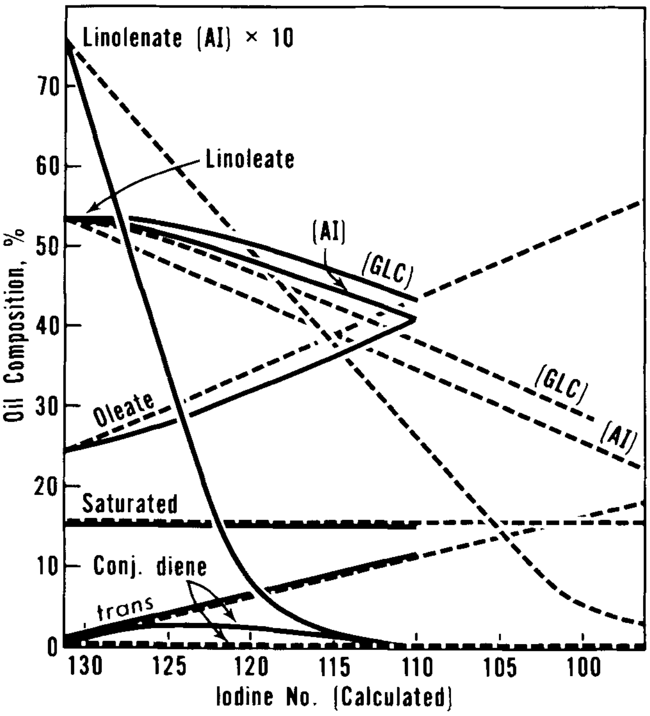

FIG. 1. Composition of soybean oil hydrogenated with copper-chromite (——) and nickel (- - - -) catalysts.

Winterization

1. To produce 20 hr cold test oil, 200 g batches of hydrogenated bleached soybean oil (HBSBO) in 250 ml beakers were crystallized for two days in a cold box regulated to an air (circulating) temperature of 4 C. The winter oil was then separated from the stearine by vacuum filtration through Whatman filter paper No. 1 in a Buchner funnel in the same cold box at 4 C.

2. To produce 5.5 hr cold test oil, 200 g batches of HBSBO in 250 ml beakers were crystallized in a cold box regulated to an air temperature of 7 C for two days. The winter oil was then separated from stearine by vacuum filtration through Whatman filter paper No. 1 in a Buchner funnel at 7 C.

Methods

The original soybean oil and the partially hydrogenated soybean oil products were analyzed as follows:

1. Fatty acid composition was determined by GLC on methyl esters of the oil esterified with BF_3•methanol reagent (30). The equipment and method of analysis are as previously described (20), except that a 1 μl sample was injected and the column temperature was maintained at 200 C.

2. Per cent *trans* isomer was determined with a Perkin-Elmer Model 337 IR spectrophotometer according to AOCS Tentative Method Cd 14-61 (31).

3. In alkali isomerization (AI), oils were analyzed according to AOCS Official Method Cd 7-58 (31) following the procedures for conjugated and nonconjugated polyunsaturated acids to determine the percentages of linoleate and linolenate. Pure methyl linolenate prepared at the Northern Laboratory by liquid-liquid extraction and 99.5% (*cis,cis*-)methyl 9,12-octadecadienoate (The Hormel Institute) served as primary standards. GLC and AI values for linoleate in unhydrogenated soybean oil methyl esters were in agreement..

4. IV was calculated from the fatty acid composition, as determined by GLC.

5. In the cold test, AOCS Official Method Cc 11-53 (31) requires that an oil remain clear after 5.5 hr immersion in ice water. Such oils are referred to in this report as 5.5 hr oil. Oils capable of withstanding the cold test for longer times will be indicated by the length of time the oil remained clear, i.e., a 20 hr oil is one that remained clear after 20 hr immersion in ice water.

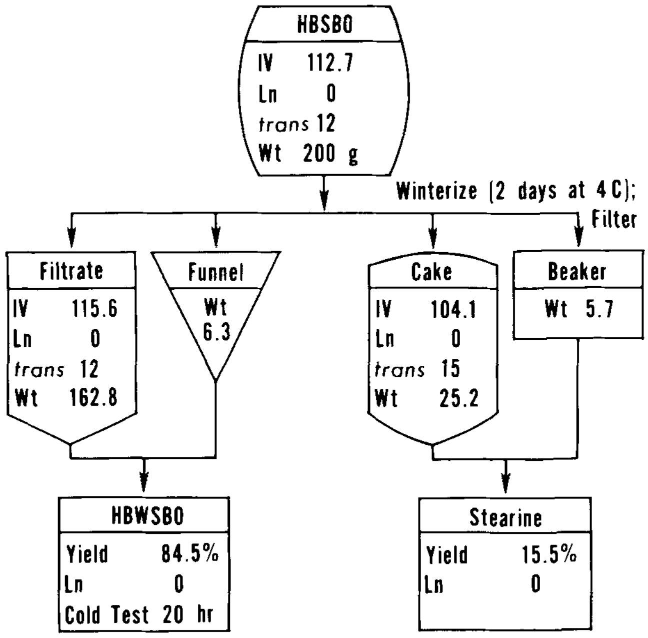

FIG. 2. Material balance flowsheet for an experimental winterization process. HBSBO, hydrogenated, bleached soybean oil; HBWSBO, hydrogenated, bleached winterized soybean oil; Ln, linolenate.

Data and Discussion

Under the conditions as described, four hydrogenations were carried out—one with 0.5% commercial copper-chromite catalyst A, one with 1.0% commercial copper-chromite catalyst B and two with 0.2% commercial Ni catalyst C.

Figure 1 depicts compositional changes resulting from the partial hydrogenation of soybean oil when the catalyst is either copper-chromite or nickel. Coincidentally, *trans* formation was substantially the same for hydrogenation with nickel catalyst at 150 C, 5 psi and with copper chromite at 170 C, 30 psi. The Cu-HSBO contained no linolenate when the IV reached about 110, but the Ni-HSBO would have to be hydrogenated to about 90 IV before all the linolenate was removed under the conditions used.

When linolenate was essentially reduced to zero from a soybean oil hydrogenated with a copper-chromite catalyst present (Cu-HSBO), 0.8% of conjugated diene was present compared to 0.2% for a Ni-HSBO containing 3% linolenate (Fig. 1). Whether the presence of nearly 1% conugated diene in a salad oil will adversely affect its flavor stability has not been established.

Although AOCS Official Method Cd 7-58 is used for determining Δ9,12 *cis,cis* octadecadienoate in unhydrogenated oils, it was used by us to analyze hydrogenated oils. The data were plotted to indicate the relative values of diene determined by GLC and AI. The difference in values indicated on Figure 1 is nonconjugatable isolinoleate formed from linolenate reduction. Our AI values may include some conjugatable dienes other than Δ9,12 *cis,cis* octadecadienoate. Nonconjugatable diene is not reduced with copper chromite but generally is with nickel. The amount of this isolinoleate increased from zero initially to a nearly constant amount for both catalysts over the IV range of our tests. Under the hydrogenation conditions used and in the IV range of our tests, neither catalyst hydrogenated monoenes to saturates. Therefore, neither would be expected to hydrogenate nonconjugatable isolinoleate since the two widely separated double bonds therein should be comparable in activity to those of monoenes.

Initially, winterization tests were conducted by crystallizing 10 lb batches of hydrogenated, bleached soybean oil at 1-3 C for two days and filtering by gravity through several layers of cheesecloth (29). Winter oil yields obtained by this method were inconsistent, however, probably because of temperature variations, viscosity of the cold oil and the varied amount of oil entrapped on the cheesecloth. Another method, crystallization for two days in a temperature-regulated cold box followed by centrifugation in a refrigerated centrifuge, also gave inconsistent results, probably because of oil entrained in the stearine and incomplete decanting of the oil.

Partially hydrogenated oil crystallized and filtered according to the methods described in Experimental Procedures gave reproducible winter oil yields that consistently passed the cold tests. There appeared to be no difference in filtration rates for oils hydrogenated with copper or nickel catalysts to the same IV.

The overall process to produce a salad oil is illustrated by a typical material balance flowsheet (Fig. 2) on the basis of the winterization method to produce 20 hr cold test oil. The refined and bleached soybean oil used for hydrogenation had an IV of 131.2, linolenate content of 7.2% and *trans* content of 1.2%. After hydrogenation of the soybean oil with copper-chromite catalyst until essentially all of the linolenate was removed, the calculated IV had dropped to 112.7 and the *trans* increased to 12%. The oil was then bleached. This copper hydrogenated, bleached soybean oil (Cu-HBSBO) was liquid at room temperature but needed to be winterized to pass the cold test.

A material balance was made for the winterization step. Two hundred grams of partially hydrogenated and bleached soybean oil was winterized and after two days at 4 C, 162.8 g of liquid oil filtrate and 25.2 g of stearine filter cake were recovered. A semisolid (5.7 g) was retained on the sides of the inverted beaker—about 2.8% of the total. Analysis of this small amount of material indicated that it consisted of both winter oil and stearine. Liquid oil (6.3 g) was recovered from the funnel and filter paper by extracting with acetone (total recovery 200 g); 84.5% was recovered as hydrogenated, bleached winterized soybean oil (HBWSBO), which remained clear after 20 hr at ice water temperature. The recovered stearine was 15.5%.

With our winterization methods larger quantities of winter oil were recovered from Cu-HSBO compared to reported (13) yields. This difference is probably due to a lower amount of winter oil being entrained in the stearine filter cake with our equipment and method or to differences in hydrogenation, or both. Bailey (22) reported a similar difference between yields from solvent and nonsolvent commercial winterizations of cottonseed oil.

The relationship between linolenate content and winter oil yield is shown in Figure 3. When nickel was the hydrogenation catalyst, the yield of both 20 hr and 5.5 hr winter oil decreased from the start of hydrogenation and at a greater rate below the 3% linolenate level than above for the 20 hr Ni-HSBO. For Cu-HSBO the winter oil yields decreased less with reduction in linolenate compared to Ni-HSBO.

A high linoleate content is considered desirable in salad oils. Previous authors (7-9,12,20) have confirmed the higher linoleate values obtained by AI in Cu-HSBO compared to Ni-HSBO. Cu-HSBO contained 51% linoleate by AI, whereas the linoleate in the Ni-HSBO was reduced to 36% at the same linolenate content of 3% (Fig. 1). The unhydrogenated soybean oil contained 53% linoleate. More in contrast were the linoleate values when linolenate was reduced to 0.5%. At this level Cu-HSBO contained 47% linoleate by AI while Ni-HSBO contained only 26%.

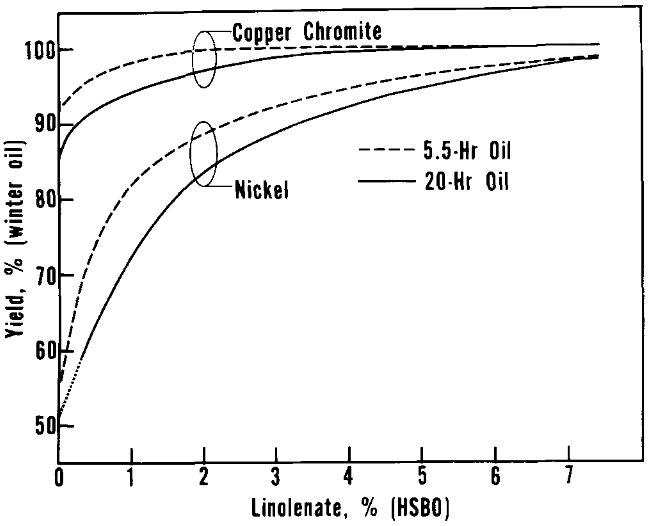

FIG. 3. Relation of linolenate content to winter oil yield of copper chromite-hydrogenated soybean oil (Cu-HSBO) and nickel-hydrogenated soybean oil (Ni-HSBO).

For a Cu-HSBO essentially free of linolenate, soybean oil was hydrogenated to an IV of 112. Yield of 20 hr winter oil was 88% and the winter oil at this IV contained 11% *trans* isomers. The IV, per cent *trans* and winter oil yield of this product were all similar to those of a commercial nickel hydrogenated oil with 3% linolenate but not the linoleate values—45% for Cu-HSBO and 40% for Ni-HSBO. When the Ni-HSBO was hydrogenated and winterized to the extent that essentially all the linolenate was removed (0.3%), only 60% 20 hr winter oil was recovered, the IV was very low (96), 19% *trans* isomers were formed and the linoleate and oleate contents were 22% and 56%, respectively.

ACKNOWLEDGMENTS

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