Hydrogenation of Oxidized Soybean Oil

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Portions of refined and bleached soybean oil were stored at various temperatures for various lengths of time, then hydrogenated to 70 iodine value (IV) to find the effect of peroxides on the rate of hydrogenation and on characteristics of hydrogenated product. Samples were treated up to 3 wk at up to 65°C and provided samples with peroxide values (PV) of up to 358. All samples were analyzed, hydrogenated, and reanalyzed. Peroxides affected the fatty acid composition as determined by gas chromatography, the calculated iodine value based on fatty acid composition, and rate of hydrogenation. Peroxides also affected the selectivity of hydrogenation and slope of the solids curve in hydrogenated products.

KEY WORDS: Fatty acid composition, gas chromatography, hydrogenation, hydrogenation rate, hydrogenation selectivity, iodine value, oxidized oil, peroxide value, solid-fat index (SFI), soybean oil.

Commercial hydrogenation of fats and fatty acids is normally accomplished in a batch reactor using metallic catalysts. The activity of the catalyst and the rate of hydrogenation can be adversely affected by such things as catalyst poisons, inhibitors, and deactivators. These materials may be constituents of the original oils, decomposition products, or may be introduced during processing (1,2).

The present work was done to find the effects of peroxides and their breakdown products on the hydrogenation process and to find at what level they become significant. Workers at Iowa State University have identified and quantified these materials in various oils (3–5).

EXPERIMENTAL PROCEDURES

A five-gallon sample of fresh refined and bleached soybean oil was obtained directly from a plant bleaching system. Two-kilogram portions were stored at temperatures of 25, 35, 45, 55, and 65°C in open glass beakers with gentle agitation, and in a hood with incandescent light. Samples were periodically removed for up to 3 wk, for analysis and hydrogenation.

Hydrogenation reactions were carried out in a laboratory-scale Parr stirred reactor at 220°C, 20 lb hydrogen pressure, with 200 g of sample and 0.02% nickel using a commercially available hydrogenation catalyst.

Peroxide values (PV) were determined using AOCS Official Method Cd-8-53 (6) with results expressed as milli-equivalents of peroxide per 1000 g of sample. Other analytical tests included Lovibond color (Cc 13 b-45), fatty acid composition (Cd 1-62), iodine value (IV) (Cd 1-25), percent *trans*-isomers (Cd 14-61), Mettler melting point (Cc 18-80), refractive index, dilatometric solids, and differential scanning calorimetry (DSC) curves using AOCS Official and Tentative methods or Anderson Clayton Foods methods.

RESULTS AND DISCUSSION

After three weeks, PV ranged from 2.4 at room temperature to 358 at 55°C. Figure 1 shows the peroxide build-up with time.

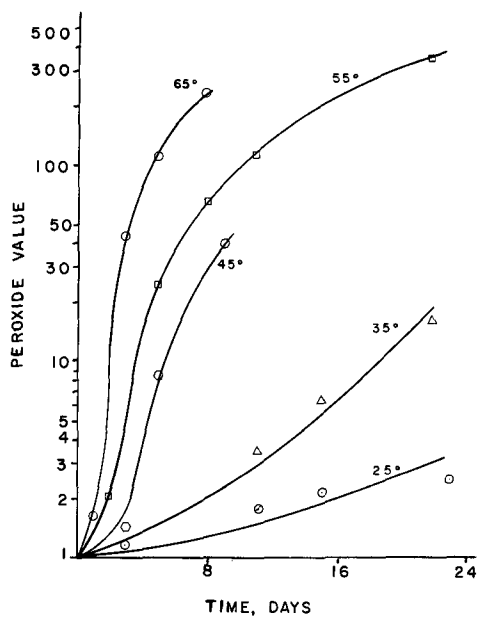

FIG. 1. Rate of peroxide increase at various temperatures.

The oxidized oils were checked for fatty acid composition before hydrogenation. Gas chromatography of the methyl esters shows an apparent decrease in the percentage of linolenic and linoleic acids with increasing PV and an apparent increase in oleic, palmitic, and stearic acids. The results are shown in Figure 2.

Iodine value calculated from the fatty acid composition

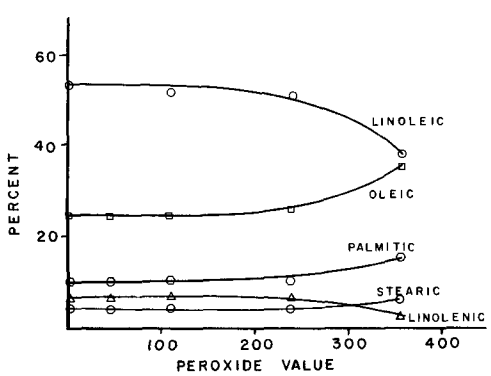

FIG. 2. Fatty acid composition of refined and bleached soybean oil.

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(Tz 1C-85) of unhydrogenated oils as a function of PV is displayed in Figure 3. The calculated IV maintained relatively constant at 130 for oils having PV values between 1.0 to 110. It dropped to 128 and 101 when the oil reached PV of 234 and 358, respectively. However, after hydrogenation, the calculated and Wijs values again correlate regardless of PV level in the starting oil. Red color on the Lovibond scale ranged from 3.5 to 2.5 on all samples before hydrogenation.

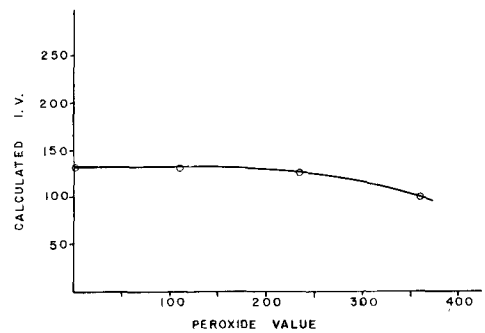

FIG. 3. Calculated iodine value of refined and bleached soybean oil.

Hydrogenation time for the original oil to reach 70 IV was 12 min and time for the oil with 358 PV to reach 70 IV was 190 min. All values obtained are plotted in Figure 4 with an R-square value of 0.89. The formula for a straight line that best fits the data is:

Hydrogenation time, min = 0.04459 (PV) + 16.2326

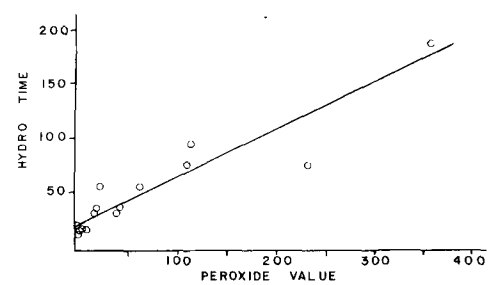

FIG. 4. Hydrogenation time in minutes to 70 iodine value.

Hydrogenated oils were checked for percent solids (Solids Fat Index). There was no significant change due to peroxide in the starting oils at values of less than 50 PV. However, high PV oils did show more of a hump in the solids curve and slightly higher solids at 40°C (104°F). Typical curves are shown in Figure 5.

Red color dropped 1.0 to 1.5 units during hydrogenation. *Trans* isomer content averaged about 48.4% at 70 IV and there was no trend due to peroxides in the starting oil. Mettler melting point averaged 40.1°C on hydrogenated samples.

A trend was found in the Selectivity Ratio of the overall results. Selectivity Ratio is defined as the ratio of the hydrogenation rate of linoleic acid divided by the rate of hydrogenation of oleic acid (7-9). Selectivity dropped from about 21 on the original oil to less than 10 at PV of 358. Computer evaluation of the data showed considerable spread with R-square of only 0.61 but the data show a definite trend (Fig. 6).

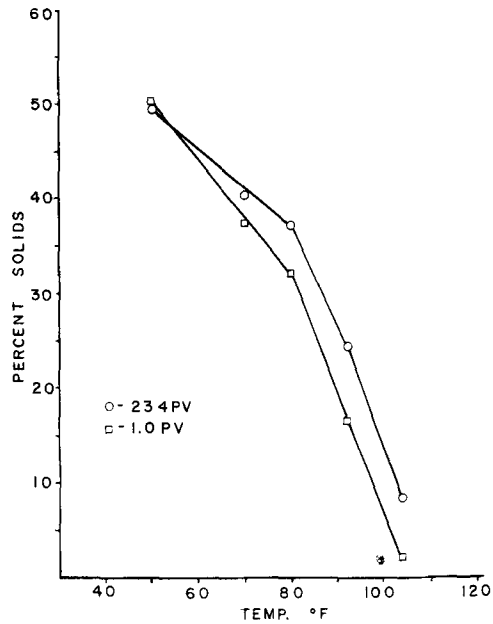

FIG. 5. Percent solids in hydrogenated fats.

Although, as a good manufacturing practice (GMP), peroxide values are carefully monitored and controlled to very low levels in oils to be hydrogenated, these results show that peroxides can have an effect on the product if allowed to become excessive. More importantly, these results show where to look in case irregularities of the types mentioned are found in soybean oil processing.

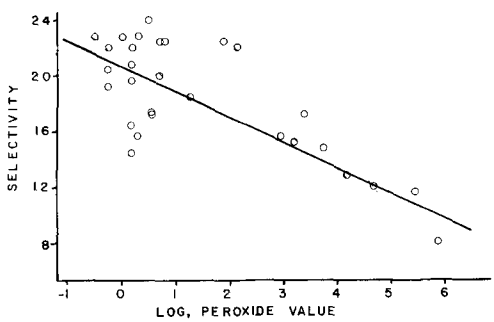

FIG. 6. Selectivity ratio vs log peroxide value.

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