The Effects of Process Variables on the Formation of *Trans*-Unsaturation During Hydrogenation[1]

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Abstract

The amount of *trans* unsaturation in 80 IV hydrogenated soybean oil produced under different reaction conditions of pressure, temperature, catalyst concentration and agitation may be calculated with good accuracy from a polynomial equation. The polynomial equation was developed from data produced by 30 experimental hydrogenations using a nonlinear equation estimation procedure with a digital computer to fit the data. The equation may be used to calculate the anticipated amount of *trans* unsaturation from the reaction conditions or select reaction conditions to produce a desired amount of *trans* unsaturation.

Introduction

The hydrogenation of vegetable oils, as practiced in the usual factory, may be accomplished in a batch stirred reactor. The operator of the reactor can vary the type of product produced by changes in the operating conditions of the reaction such as temperature and hydrogen pressure, the type and amount of catalyst, and the agitation of the reactor contents.

Each of these operating conditions has an effect on the rate and products of the reaction and the effects are interrelated as shown by Bailey (1), Albright (2), Stingley (3) and Stefanovic (4).

One result of the hydrogenation, in addition to saturation, is the isomerization of the *cis* double bonds to the *trans* form. The formation of this *trans* unsaturation or iso-oleic is concomitant with hydrogenation and is affected by the reaction conditions (5). In many hydrogenated fat products the iso-oleic or *trans* unsaturated acid is the major fatty acid present. The double bond in the iso-oleic acids may also be positionally isomerized (6). All of the *trans* isomers melt somewhat higher than the *cis* unsaturated acids but lower than the saturated. Therefore, the amount of *trans* unsaturation in a fat has an effect on the consistency of the fat, particularly at lower temperatures.

This study is an attempt to evaluate quantitatively the effect of each of the variables, pressure, temperature, rate of agitation and catalyst concentration on the formation of *trans* isomers by an empirical model derived from experimental data by use of a digital computer.

Experimental Procedures

To study these four variables, a four factor central composite designed experiment that required 30 experimental hydrogenations with the reaction conditions varied in a regular order was used (7). The 30 experiments included six replications of the central design point.

The 30 experimental hydrogenations were performed in a 1 liter Parr medium pressure apparatus. One small 3 blade, 1 in. diameter agitator at the bottom of the reactor was used and the rate of stirring varied by a controlled speed motor. The rather large sampling tube and gas inlet tube of the original apparatus was replaced by a ⅛ in. o.d. stainless steel tube that extended from the external valve system to the bottom of the reactor. This small sample tube eliminated contamination of samples and made possible the hydrogenation of 100 g samples of oil that allowed good temperature control. The temperature was controlled by an oil bath surrounding the reactor, and pressure was controlled by a double stage regulator on the cylinder of hydrogen. The catalyst reported here was a dry reduced nickel catalyst of high selectivity.

The hydrogenations were performed by heating the mix of weighed catalyst and refined and bleached soybean oil in the reactor to the desired temperature under vacuum. The hydrogenation was started by the addition of hydrogen at the desired pressure and rapidly rinsing the reactor twice with hydrogen. The

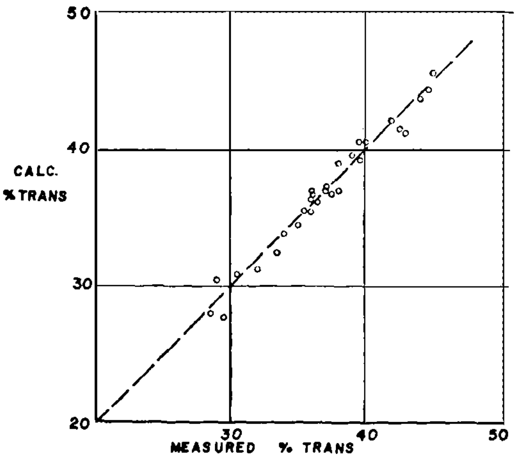

FIG. 1. *Trans*-unsaturation calculated from the polynomial equation compared to measured values.

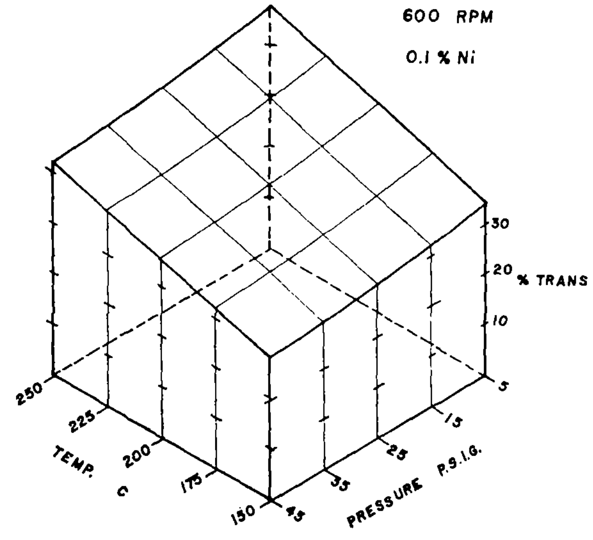

FIG. 2. The response to pressure and temperature of the amount of *trans* unsaturation formed by hydrogenation of soybean oil to 80 IV.

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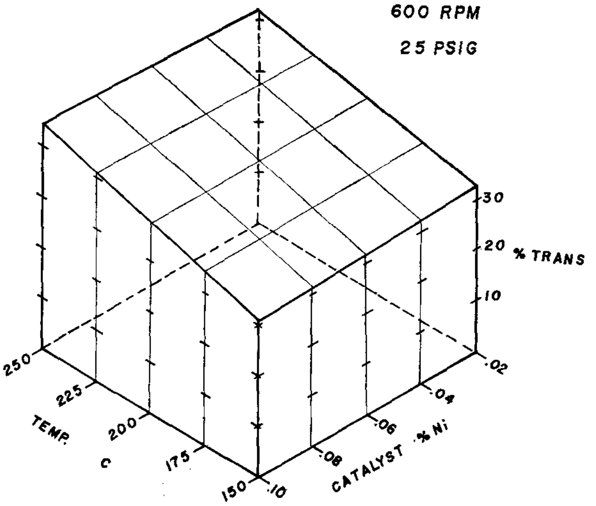

FIG. 3. The response to temperature and catalyst concentration of the amount of *trans* unsaturation formed by hydrogenation of soybean oil to 80 IV.

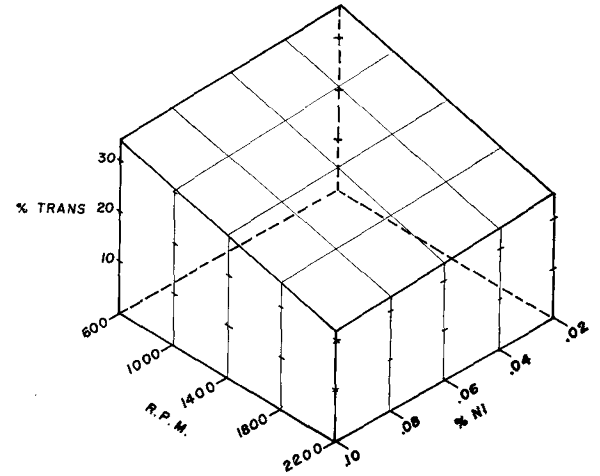

FIG. 5. The response to rate of agitation and catalyst concentration of the amount of *trans* unsaturation formed by hydrogenation of soybean oil to 80 IV.

timing was started as soon as the pressure reached the experimental conditions. Small samples, about ½ g, were withdrawn periodically and the reaction followed by refractive index decrease. Samples of hydrogenated oil of about 110, 90 and 80 IV were analyzed, the fatty acid composition determined by GLC, and *trans* measured by IR absorbance. From these data, the % *trans* isomers at 80 IV was calculated. The % *trans* unsaturation at 80 IV of each of the 30 hydrogenations under the different reaction conditions were used to calculate the constants of the second degree polynomial least squares equation (8). All two factor interactions of the conditions were used in the equation. The reaction conditions were not coded but the actual values were used.

Results and Discussion

The second degree polynomial equation that related the % *trans* unsaturation of 80 IV soybean oil and the hydrogenation conditions is:

$$\%\ trans\ (80IV) = 29.2423 - .2229P + .08614T - .007308A - 103.0256C + .001738P^2 + .2273 \times 10^{-4}T^2 + .94396 \times 10^{-6} A^2 - 2.342C^2 - .2152 \times 10^{-4}PT + .34123 \times 10^{-4}PA + .02054\ PC + .82089 \times 10^{-5}TA + .5138\ TC - .001197\ AC.$$

P is lb/sq in. H_2, T is temperature C, A is the rpm of the agitator shaft and C is catalyst as per cent nickel.

The regression coefficient R = .9863 and the plot of calculated *trans* vs. observed *trans* shown in Figure 1, indicate a very good fit of the equation to the experimental data.

It must be emphasized, this equation is an empirical equation that describes the relationship of *trans* unsaturation of 80 IV soybean oil and the reaction conditions using our experimental reactor. This equation cannot be used to predict the *trans* unsaturation in another reactor since the agitation would probably be different even if the same rpm agitator was used. This would result in a difference in the reaction (9).

The % *trans* unsaturation surface response calculated from the equation may be shown by the use of isometric projections that relate two of the factors to the amount of *trans* unsaturation produced by the hydrogenation.

Figure 2 shows the interrelation of the effects of pressure and temperature. As is well known, low pressure and high temperature produce the most *trans* and the effects are additive with the tempera-

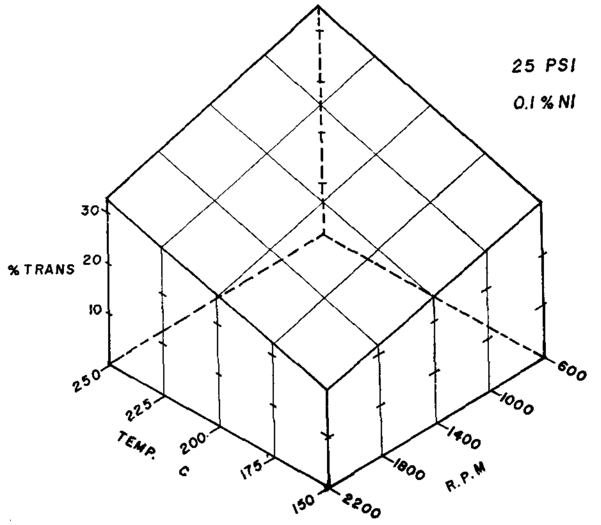

FIG. 4. The response to temperature and rate of agitation of the amount of *trans* unsaturation formed by hydrogenation of soybean oil to 80 IV.

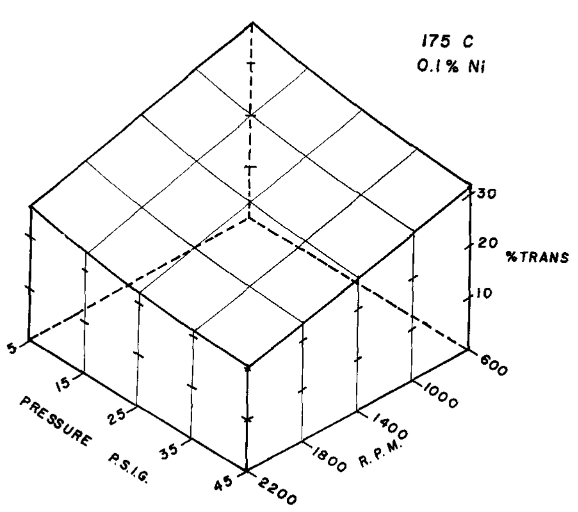

FIG. 6. The response to pressure and rate of agitation of the amount of *trans* unsaturation formed by hydrogenation of soybean oil to 80 IV.

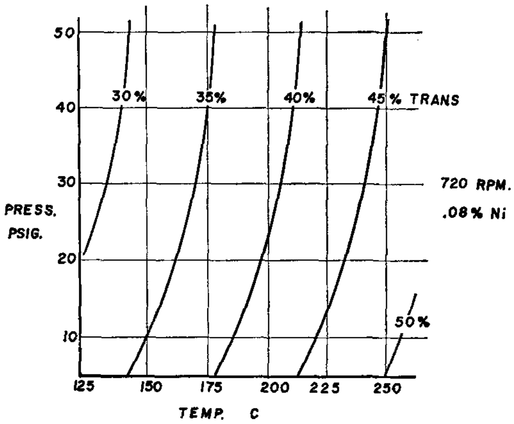

FIG. 7. Reaction conditions necessary to produce a known amount of *trans* unsaturation in soybean oil at 80 IV.

ture change causing the greatest change in the *trans* unsaturation. The effect of temperature is also greater than the effect of a change in the catalyst concentration as shown by Figure 3. It indicates the catalyst had little effect on the amount of *trans* unsaturation formed as was shown by Johnston et al. (10). However, agitation had almost as much effect as temperature as shown by Figure 4 which shows the related effects of temperature and rate of agitation.

The agitation effect is also large if related to catalyst concentration (Fig. 5) or pressure (Fig. 6).

Thus the factors that affect the production of *trans* unsaturation are temperature > agitation > pressure > catalyst concentration.

Another way the equation may be used is to find the conditions necessary to produce a desired amount of *trans*. By use of a digital computer programmed with the polynomial equation, the data necessary to obtain curves such as shown in Figure 7 are calculated. From this graph the conditions necessary to produce any desired amount of *trans* unsaturation at 80 IV is estimated. Since there are an infinite number of temperature and pressure combinations that will produce the same amount of *trans* unsaturation, the combination to use will depend on some other desired component in the mix such as the amount of saturated acids. With this restriction introduced, the reaction conditions necessary to produce both the desired *trans* and saturated may be estimated.

Although the equation developed by this study is empirical, it is useful. Similar equations could be developed for full scale hydrogenation equipment. These equations would permit the calculation of the conditions necessary to produce a desired product without experimental hydrogenations in small equipment.

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