

Correlations for *Trans*-isomer Formation during Partial Hydrogenation of Oils and Fats

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ABSTRACT

Two empirical models are proposed to correlate the amount of *trans*-isomers formed during the partial hydrogenation of oils and fats as a function of the degree of hydrogenation and process variables. From minimal experimental data, constants for these models can be obtained and used to interpolate or extrapolate the *trans*-isomer data to predict the amount of *trans*-isomers formed during a partial hydrogenation or to select processing conditions for a desired amount of *trans*-unsaturation. The application of these models has been demonstrated using hydrogenation data for soybean and rapeseed oils.

INTRODUCTION

In any partial hydrogenation of fats and oils, many simultaneous and consecutive reactions occur which cause geometric isomerization of a part of the remaining double bonds. The amount of geometrically isomerized double bonds present in a partially hydrogenated product has a significant effect on its physical properties. The extent of isomerization for a given degree of hydrogenation depends strongly on the hydrogenation conditions (1-4). The reactions occurring during hydrogenation are controlled by two primary factors which Stingley and Wrobel (3) referred to as hydrogen availability and hydrogen demand. Hydrogen demand may be defined as the potential rate at which the unsaturated bonds of an oil or fat combine with hydrogen to form saturated bonds. This is controlled by the kinetics of the hydrogenation reaction when the mass transfer resistance at the gas-liquid and liquid-solid interphase is negligible. Hydrogen availability, on the other hand, is dependent on the mass transfer rates at the two interfaces, and it controls the course of the hydrogenation reaction.

For a given hydrogenator, the hydrodynamics of the gas-liquid and liquid-solid phases is fixed due to the design of the reactor, agitator and gas sparger. If catalyst activity is also fixed, then temperature (T), pressure (P) and catalyst concentration (C) are the only process variables which govern hydrogen availability and demand during a hydrogenation reaction. The directional effect of these process variables on the hydrogen concentration and selectivity, which expresses the preferential hydrogenation of polyenoic chains over monoenoic chains, is given in Table I. It is interesting to note that the conditions which lower hydrogen concentration in the reaction system simultaneously increase the selectivity and *trans*-isomer formation. Zajcew (4) pointed out that for the hydrogen transport rate to have any effect on the *trans*-contents, it is necessary that isomerization have a different dependence on hydrogen concentration than the saturation of the double bonds. Since it is known that hydrogen deficiency at the catalyst surface encourages isomerization relative to the saturation of double bonds, care must be taken to account for effects due to the variation of *trans*-isomers on the properties of oil while selecting processing conditions to obtain a desired selectivity.

Since all process variables (T, P and C) affect hydrogen availability during hydrogenation, within practical limits one can establish a series of P-T-C relationships which would result in the same type of reactions. By using appropriate models, a limited amount of experimental data can

be used to obtain the correlations from which additional values can be predicted by interpolation and extrapolation of the data.

PREVIOUS MODELS

The earliest attempt to correlate *trans*-isomer data with process variables to enable interpolation was made by Stingley and Wrobel (3), who defined the Hydrogenation Index as the percentage of double bonds isomerized to the *trans*-configuration per unit double bond saturation. This concept was a significant step which probably led to the defining of the Isomerization Index by Albright, Allen and Moore (2) and Specific Isomerization by Coenen (5).

Albright, Allen and Moore (2) reported a mathematical model for the calculation of isomerization index for partially hydrogenated oils using a digital computer. Their model was very complex and required several empirical modifications before it could be applied.

Allen and Covey (6) correlated *trans*-isomers formed for a given degree of hydrogenation with process variables using a second degree polynomial equation. While the scope of their equation is limited to their data, similar equations can be developed for other hydrogenations.

PROPOSED MODELS

Two empirical methods are proposed for correlating the *trans*-isomer data with the degree of hydrogenation and the process variables. By using minimal experimental data, constants for these models can be obtained. These models can be used to interpolate or extrapolate the experimental data to calculate the anticipated amounts of *trans*-isomers or to select conditions for a desired amount of *trans*-unsaturation. The application of the proposed models is demonstrated using the hydrogenation data obtained from the technical bulletins of a commercial catalyst for soybean oil and rapeseed oil (7).

Model I

This model is based on the concept of Specific Isomerization Index (SII), which was first used by Puri and deMan (8) to correlate the *trans*-isomer data for rapeseed oil hydrogenation.

The SII is defined as the number of *trans*-double bonds formed per unit rate of iodine value reduction. Characteristics of SII are found using a variety of hydrogenation data obtained on different reactors for different oils and catalysts. It is found that for all data at low reaction rates (<1.0 IV/min), SII decreases as the variables (P, T or C) increase. At high reaction rates, the rate becomes dominantly mass transfer controlled, and the effect of process

TABLE I
Effect of Process Variables on *Trans*-isomer Formation

Increase of	Effect on	
	Hydrogen concentration	<i>Trans</i> -isomer formation
Temperature	-	+
Pressure	+	-
Catalyst	-	+

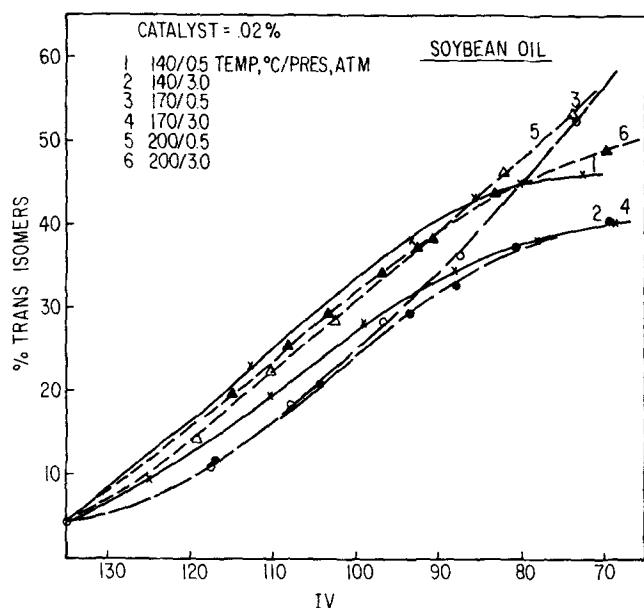
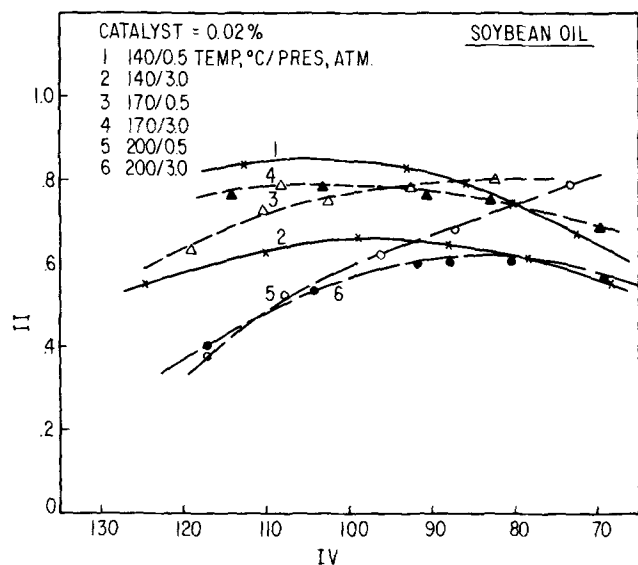
FIG. 1. *Trans*-isomers formed at different processing conditions.

FIG. 2. Isomerization index calculated for different processing conditions.

variables on it diminishes. The dependency of SII with the process variables in those cases does not follow any fixed trends.

The characteristics of the SII offer an advantage in representing the experimental data. Figure 1 shows the data of *trans*-isomers as a function of unsaturation of soybean oil for different temperature and pressure conditions. From this plot no definite conclusions can be made on the effect of temperature and pressure on *trans*-isomer formation. Nor can generalizations be made when one uses the isomerization index concept. This is illustrated in Figure 2. The effects of temperature and pressure are distinctly shown on the SII vs. IV plot (Figure 3).

A plot of the type shown in Figure 3 can be used to interpolate SII data for any given IV to obtain a desired SII, or inversely for a given SII and IV, this plot can give approximate hydrogenation conditions.

For exactness the SII data can be correlated with the IV and process variables using nonlinear multiple regression method on a digital computer. The following equations

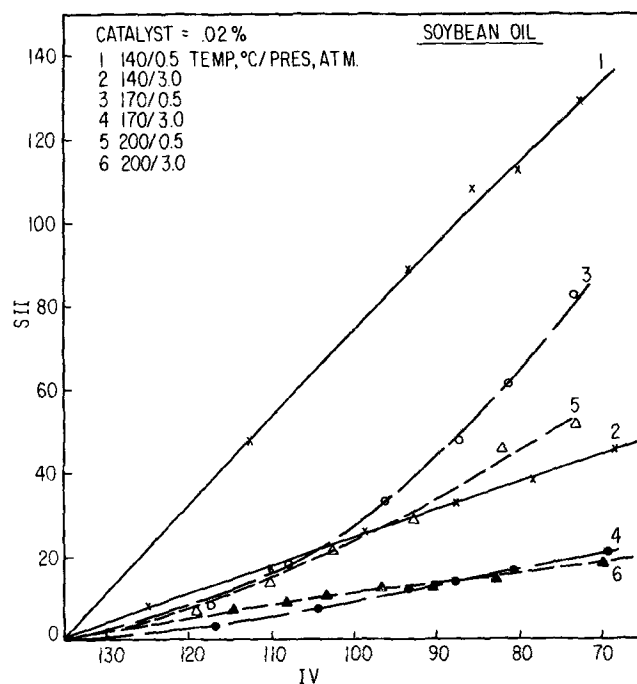


FIG. 3. Specific isomerization index calculated for different processing conditions.

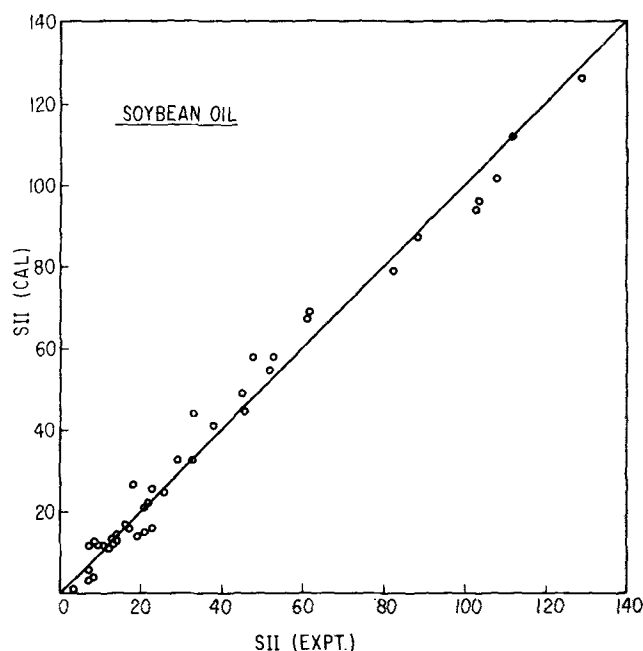


FIG. 4. Specific isomerization index calculated from equation 1 compared to experimental values.

were obtained:

Soybean oil

$$\text{SII} = 934 - 3.8 \text{ IV} - 6.2 \text{ T} + 0.012 \text{ T}^2 - 6.8 \text{ P} + .012 \text{ IV X T} + .029 \text{ IV X P} + .018 \text{ T X P} \quad (1)$$

Rapeseed oil

$$\text{SII} = 424.5 - 0.93 \text{ IV} - 2.95 \text{ T} + .007 \text{ T}^2 - .79 \text{ P} \quad (2)$$

P is psig hydrogen pressure and T is temperature C. The regression coefficients for the soybean and rapeseed equations were 0.97 and 0.94, respectively. The plots of calculated SII vs. observed SII are shown in Figures 4 and 5, indicating a good fit of the equations to the experimental data. The typical SII surface response plots calculated from these equations are shown in Figures 6 and 7 for a few

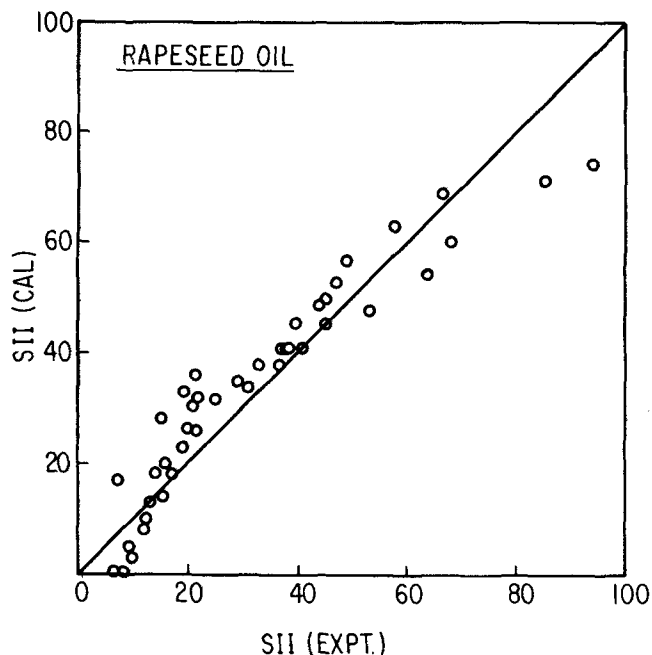


FIG. 5. Specific isomerization index calculated from equation 2 compared to experimental values.

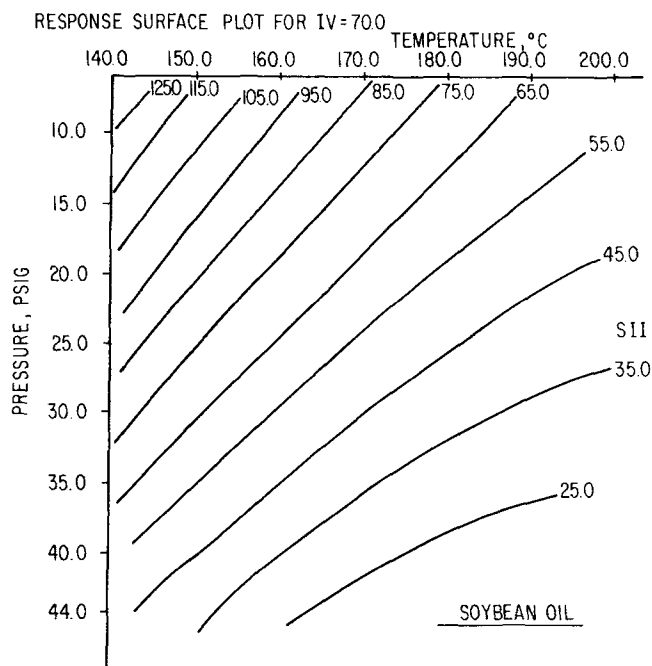


FIG. 6. Response surface plot calculated from equation 1 at 70 IV.

selected, partially hydrogenated oils. From these plots the conditions necessary to produce an oil of desired SII for a given degree of unsaturation can be obtained.

It must be pointed out that the equations presented here are empirical and true for the data with which they were developed. Similar equations could be developed for other data and used to calculate the conditions necessary to produce partially hydrogenated oils containing a known quantity of *trans*-isomers without resorting to experimental hydrogenations.

Model II

For a given hydrogenation, the rate at which *trans*-isomers form during reduction can be correlated with the

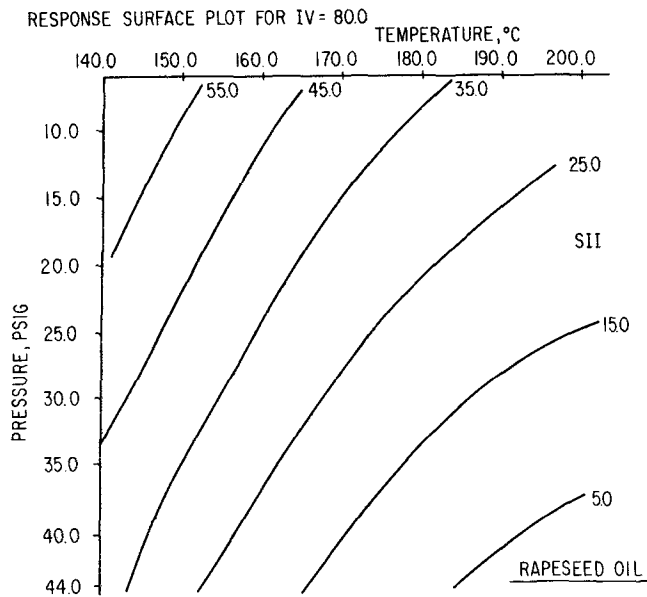


FIG. 7. Response surface plot calculated from equation 2 at 80 IV.

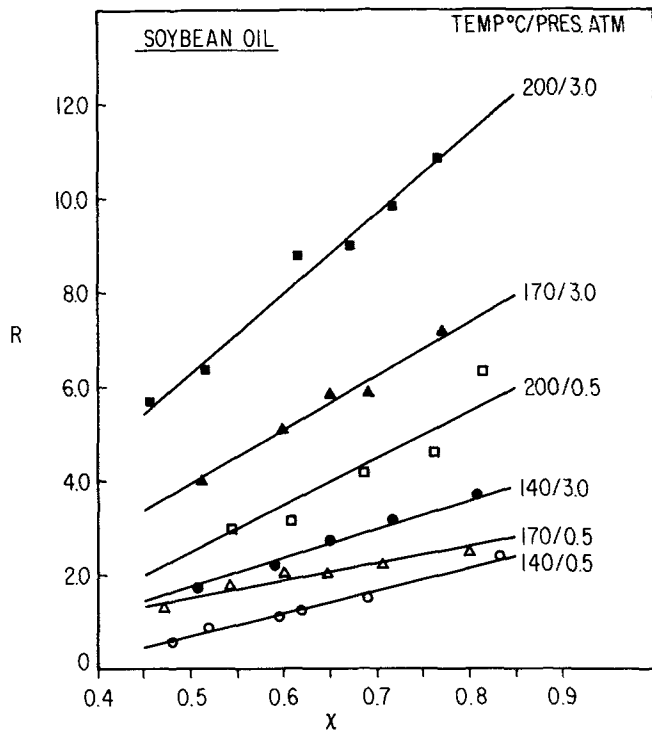


FIG. 8. Plot of R vs. X for SBO at different processing conditions.

degree of unsaturation of the oil using the following empirical equation:

$$\Delta \text{Trans}/t = \chi (1-\chi) (m\chi + C) \tag{3}$$

where

- ΔTrans = Hydrogenated *Trans* % - Original *Trans* %
- χ = Hydrogenated IV/Original IV
- t = Reaction time, min
- m and C = Constants

By knowing constants m and C , one can find the rate of *trans*-isomer formation for a given hydrogenation using equation (3). If more data are available, confidence in the values m and C will be increased.

Rearranging equation (3) takes the form of a linear

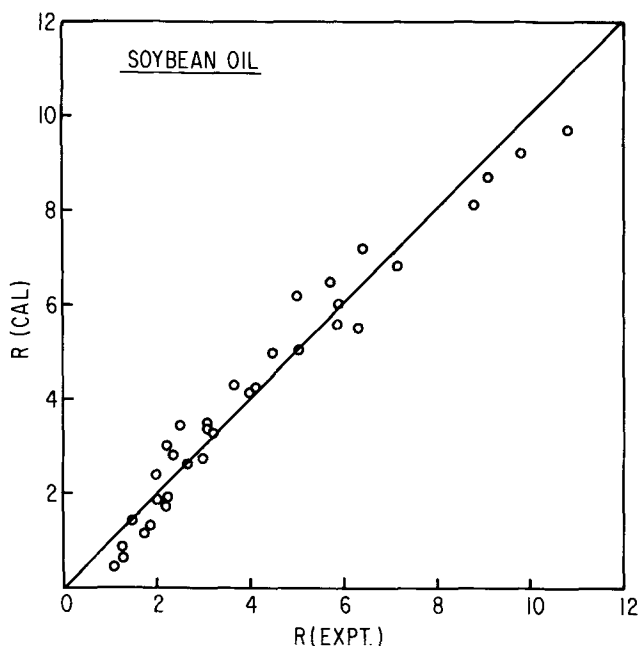


FIG. 9. Calculated R from equation 5 compared to experimental values.

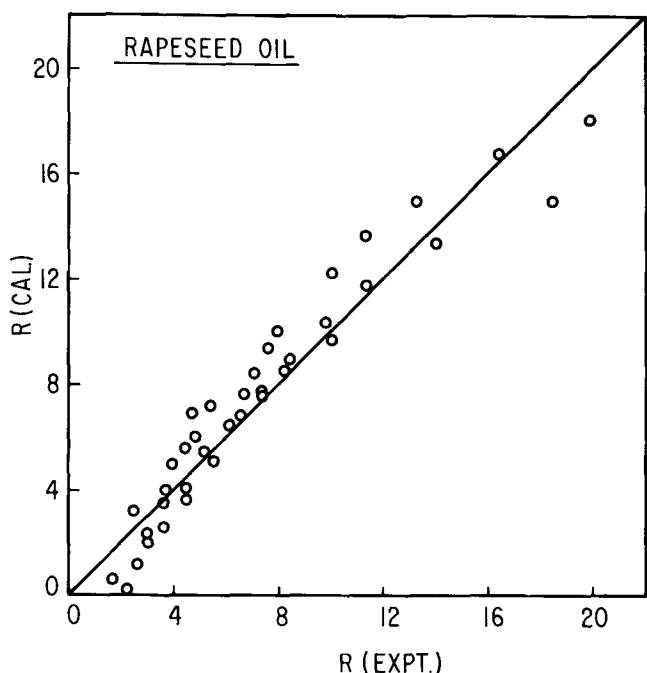


FIG. 10. Calculated R from equation 6 compared to experimental values.

equation:

$$R = \Delta \text{Trans}/(t) (\chi) (1-\chi) = m \chi + C \quad (4)$$

from which constants m and C can be calculated with a minimum of two data points. More data, however, will give more representative values for these constants.

The application of equation (4) was tested for the soybean and rapeseed oil data mentioned earlier. Figure 8 shows the soybean oil data plotted as R vs. χ . It was found that for values of χ between 0.5 and 0.85, which is of commercial interest for edible oil hydrogenation, the data were adequately represented by the linear model with multiple correlation coefficient greater than 0.95 in all the cases. This simple model can be used to interpolate or extrapolate *trans*-isomer data for a given set of processing

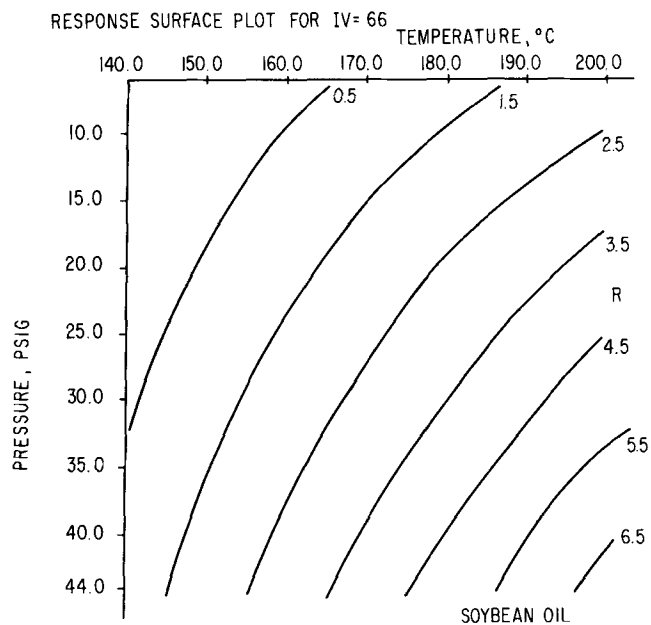


FIG. 11. Response surface plot calculated from equation 5 at 66 IV.

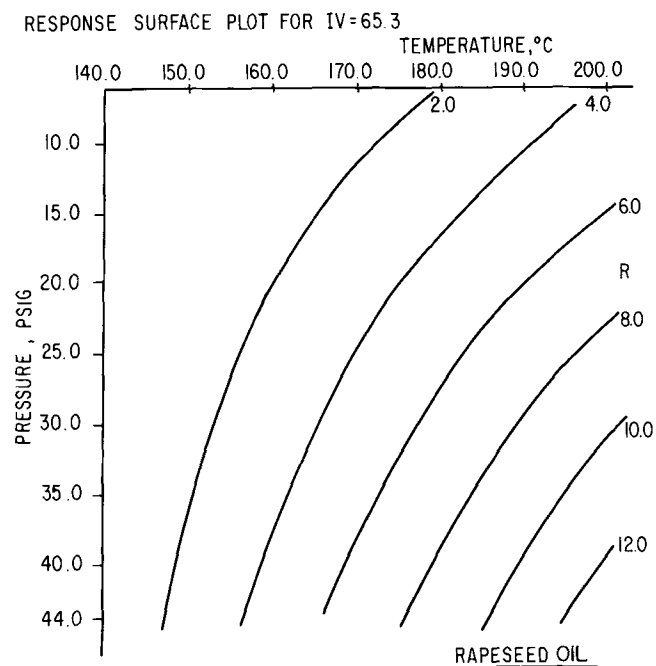


FIG. 12. Response surface plot calculated from equation 6 at 65.3 IV.

conditions, provided at least two experimental data points are available. This model is useful for plant applications where it may not be possible to perform several experiments to obtain the data for a given range of unsaturations.

The application of this method is further extended by including the pressure and temperature terms in the multiple regression equations to obtain models in which the rate of *trans*-isomer formation is correlated with the degree of hydrogenation and the process variables. The models obtained for the soybean oil and rapeseed oil hydrogenation are as follows:

Soybean oil

$$R = -11.06 + 10.07 \chi + 0.037 T - 0.15 P + .014 TP \quad (5)$$

Rapeseed oil

$$R = 3.31 + 33.2 \chi + .073 T - .38 P + .0037 TP \quad \text{---(6)}$$

where

χ = Hydrogenated IV/Original IV
T = °C
P = psig

The multiple correlation coefficients for the two cases were 0.97 and 0.95, respectively. The plots of calculated R are shown in Figures 9 and 10, indicating a good fit of equations to the experimental data. The surface response plots calculated from these equations for a few selected IVs are shown in Figures 11 and 12. These plots can be used in a similar manner as the SII plots. Again, these plots are empirical and true only for the data from which they were developed.

ACKNOWLEDGMENT

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REFERENCES

1. Swern, D., Ed., "Bailey's Industrial Oil and Fat Products," 3rd ed., Interscience Publications, New York, 1964.
2. Albright, L.F., R.R. Allen, and M.C. Moore, JAOCS, 47:295 (1970).
3. Stingley, D.V., and R.J. Wrobel, Ibid. 38:201 (1961).
4. Zajcew, M., Ibid. 37:11 (1960).
5. Coenen, J.W.E., "Margarine Today," Proceedings of a Seminar held at Dijon University, Leideu, E.J. Brill, 1970.
6. Allen, R.R. and J.E. Covey, JAOCS 47:494 (1970).
7. Nysel DM-3 Brochures, The Harshaw Chemical Co., Cleveland, Ohio 44106.
8. Puri, P.S. and J.M. deMan, "Hydrogenation of Rapeseed Oil," Paper presented at the 67th Annual Session of the American Oil Chemists' Society, Chicago, September 1976.

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