

Behavior of Hydrogenation Catalysts. I. Hydrogenation of Soybean Oil with Palladium¹

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ABSTRACT

A statistical method for evaluation of catalysts was used to determine the behavior of palladium catalyst for soybean oil hydrogenation. Empirical models were developed that predict the rate, *trans*-isomer formation, and selectivity over a range of practical reaction conditions. Two target iodine value (IV) ranges were studied: one range for a liquid salad oil and the other for a margarine basestock. Although palladium has very high activity, it offered no special advantage in *trans*-isomer formation or selectivity. Palladium can substitute for nickel catalyst, at greatly reduced temperature and catalyst concentrations, for production of salad oil or margarine basestock from soybean oil.

INTRODUCTION

An evaluation of catalyst behavior for the hydrogenation of vegetable oils is required before one can introduce a catalyst into production-scale operation. In the present case, a palladium catalyst was compared to nickel catalyst to determine whether palladium could be used economically for hydrogenating soybean oil. Two specific properties were desired of the catalyst: greater selectivity and more isomerization control.

The literature to date indicates that palladium might have the desired selectivity and isomerization characteristics. Rylander (1) has reviewed platinum-group catalysts and concludes that palladium has high reactivity and selectivity. A more recent review of catalysts by Gray and Russell (2) agrees with those conclusions. In two other studies, however, where catalysts were compared, the authors found lower selectivity for palladium (3,4) than for nickel. None of the researchers used experimental conditions that could be compared directly. Nor did they attempt to define the optimal conditions for palladium use.

Although the available literature points to high selectivity and activity for palladium, the reports available apply only to the conditions used in those experiments. A comparison method for determining catalyst behavior is needed. For similar catalysts incorporating the same metal, methods such as the AOCS Standard Catalyst Activity Method might be used to evaluate catalyst behavior (5). This method is useful when a large data base exists and the differences between catalysts are relatively small. In the present case, however, the catalysts and the conditions at which they perform well are known to be significantly different.

To evaluate the behavior of 5% palladium-on-carbon, a catalyst-screening survey is needed that both estimates optimum conditions for the catalyst and allows comparison with other metal catalysts. It is also more desirable to estimate the behavior of the catalyst over a wide range of conditions than to evaluate it at a very few fixed, arbitrary conditions. Such a comprehensive catalyst-screening survey requires that a statistical experimental design be used so that several dependent variables can be studied with a minimum number of experiments. Unfortunately, few design evaluations have been reported in the literature of the vegetable oil industry.

This paper describes a statistical evaluation method for estimating the performance of a palladium catalyst at conditions suitable for large-scale hydrogenation of soybean oil. Several factors were considered in judging performance: reaction rate, selectivity, isomerization, operating conditions, amount of catalyst and reusability. A comparison was made with nickel catalysts in general, and the implications of this method's results were considered for the suitability of palladium catalyst in production of salad oil or hardened fats.

EXPERIMENTAL

In creating a statistical evaluation method and associated models, a two-level factorial design was chosen with three independent variables and a duplicate center point (6). The independent variables of temperature, hydrogen pressure and catalyst concentration defined the factor space, and the variables of rate, *trans*-isomer content, fatty acid composition and melting characteristics were observed as responses.

A series of 10 batches was required for the design hydrogenations. To minimize the number of batches required, samples were withdrawn at two IV levels (114 ± 4 and 66 ± 4). This, in effect, doubled the design but allowed for better estimates of selectivity and catalyst behavior. Data collected on each batch were evaluated statistically to obtain the relationship of the dependent variables to the independent variables.

All reactions were run in a lab-scale 600 ml Parr reactor at a fixed rpm. The stirrer speed was chosen to approximate that called for by the AOCS Standard Catalyst Activity Method. All batches were run with refined and bleached soybean oil and with commercially available 5% palladium-on-carbon catalyst. Iodine value was estimated during reaction by measuring pressure drop in a hydrogen supply tank. Samples were withdrawn through a sampling tube and the catalyst removed by filtration. Analyses were done by standard AOCS methods; the results are given in Tables I and II.

The models were developed using the SAS statistical package. Each independent variable was transformed to a common scale with a range of -1 to +1 according to the equation: $(\text{high value} - \text{median value})/(\text{range})$. This method of coding simplifies the statistical analysis and results in coefficients that are in proportion to the contribution of that term to the value of the dependent variable. Step-wise regressions were run, and the best-fit models were chosen on the basis of the largest R^2 and lowest-mean-square error. It also was found that coding the observed IV's and including an SIV term improved the models [$\text{SIV} = (\text{actual IV} - \text{mean IV})/(\text{standard deviation})$]. Reasonable models were found for each of the measured responses.

RESULTS AND DISCUSSION

Catalyst Activity

Preliminary experiments with soybean oil in our laboratories confirmed that palladium-on-carbon catalyst was active in liquid soybean oil down to room temperature even

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TABLE I

Hydrogenation Data for Soybean Oil: Salad Oil Target

Batch number	Reaction conditions			Reaction rate (IV/min)	Final IV	% <i>trans</i> isomers	Selectivity		Fatty acid composition			
	Temp. (°C)	Pressure (psig)	Catalyst (% Pd)				Sr ^a	Sd ^b	C18:0	C18:1	C18:2	C18:3
1	93	50.0	.0005	1.61	116.7	29.9	1.9	20.5	3.8	36.3	43.0	4.7
2	60	27.5	.00275	.63	117.8	22.2	1.7	8.3	4.3	34.1	43.9	5.3
3	93	5.0	.0005	.48	116.7	28.5	1.3	18.0	3.3	34.4	43.2	6.0
4	27	50.0	.0050	.21	118.6	15.3	1.7	5.5	4.8	33.7	44.4	5.5
5	27	5.0	.0050	.08	113.6	18.2	1.9	7.4	4.6	35.6	42.4	4.6
6	27	50.0	.0005	.28	114.9	25.0	2.5	12.4	4.0	34.6	45.2	4.3
7	93	50.0	.0050	3.16	110.5	20.7	1.7	6.1	5.3	37.7	39.7	4.3
8	60	27.5	.00275	.67	114.6	24.4	2.3	8.3	4.4	35.2	43.7	4.3
9	93	5.0	.0050	1.17	113.5	22.4	1.6	12.0	4.1	35.9	41.2	5.0
10	27	5.0	.0005	.05	115.9	30.7	2.7	18.2	3.8	35.0	45.3	4.1
Average 115.3												

^aLinolenic selectivity.^bLinoleic selectivity.

TABLE II

Hydrogenation Data for Soybean Oil: Margarine Basestock Target

Batch number	Reaction conditions			Reaction rate (IV/min)	Final IV	% <i>trans</i> isomers	Fatty acid composition				Solid content index					
	Temp. (°C)	Pressure (psig)	Catalyst (% Pd)				Sd ^a	C18:0	C18:1	C18:2	C18:3	50F	70F	80F	92F	F102
1	93	50.0	.0005	1.70	66.2	51.6	27.4	15.2	72.1	1.1	1.3	63.8	53.7	49.5	34.9	20.8
2	60	27.5	.00275	.60	68.5	56.8	53.7	10.9	76.7	.6	.5	64.6	51.9	45.5	27.5	12.6
3	93	5.0	.0005	.50	68.9	57.7	50.9	12.3	75.2	.5	.7	65.9	53.9	47.8	30.1	13.9
4	27	50.0	.0050	.28	68.2	45.1	43.0	12.3	75.4	.7	.6	48.6	34.2	30.3	20.5	12.8
5	27	5.0	.0050	.12	64.4	51.9	70.7	14.2	73.4	.0	.6	64.6	52.7	47.8	37.8	18.5
6	27	50.0	.0005	.27	65.1	54.0	12.6	15.3	67.4	5.1	.3	66.9	55.3	50.2	33.3	17.8
7	93	50.0	.0050	2.67	54.0	38.0	9.3	23.6	59.7	2.9	1.0	73.3	70.3	68.4	60.3	45.1
8	60	27.5	.00275	.58	63.9	54.8	21.1	14.5	70.8	2.0	.4	69.3	60.0	55.3	38.6	20.6
9	93	5.0	.0050	1.05	64.2	55.1	16.0	13.5	65.1	3.7	1.3	68.4	59.6	54.8	39.2	20.3
10	27	5.0	.0005	.05	64.7	51.9	12.0	17.3	66.3	4.0	.3	66.7	59.6	55.6	50.2	22.8
Average 64.8																

^aLinoleic selectivity.

at low metal concentrations. Determination of the reaction conditions that would give reasonable reaction times was one objective of the study. Therefore, the ranges of parameters chosen reflect a balance between catalyst amounts and reaction temperature. Palladium is much more active than nickel catalysts for hydrogenation of soybean oil; thus, much less metal is required and operating temperatures can be below the normal operating range for nickel catalysts. At temperatures above 150 C and with more than 0.004% nickel, reaction rates of 0.2 to 3.0 IV/min can be obtained; palladium catalyst can achieve the same rates between 27 and 93 C at only 0.00025% palladium. The minimum palladium catalyst level, however, has unacceptably slow reaction rates for the ranges of other independent variables used here. Development of a reaction rate model was an important result for use in determining an economical palladium concentration for the two different IV target ranges.

A satisfactory rate model was obtained based on the experimental data for each of the target IV ranges. A convenient aspect of the model is that the coefficients in the model equation each represent the proportional contribution of that term to the response. Thus, although positive changes in temperature, pressure and catalyst concentration all increase the rate, the coefficients from the model equa-

tion indicate that the contributions of temperature and pressure are more significant than the contribution of the catalyst concentration. Furthermore, inclusion of the SIV term allows for correction of the rate when the final IV is near the target. Separate rate equations were developed for each of the two different target IV's at which samples were taken.

$$\begin{aligned} \text{Rate (IV/min)} &= 0.652 - 0.181(\text{SIV}) + 0.202(\text{SIV})^2 \\ &+ 0.602(\text{T}) + 0.322(\text{P}) + 0.043(\text{C}) \\ &+ 0.226(\text{T})(\text{P}) + 0.144(\text{T})(\text{C}) \\ (114 \text{ IV}) \quad &R^2 = 0.999 \quad [1] \end{aligned}$$

$$\begin{aligned} \text{Rate (IV/min)} &= 0.782 + 0.650(\text{T}) + 0.400(\text{P}) \\ &+ 0.200(\text{C}) + 0.305(\text{T})(\text{P}) \\ &+ 0.180(\text{T})(\text{C}) \\ (66 \text{ IV}) \quad &R^2 = 0.977 \quad [2] \end{aligned}$$

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Encoding equations:

$$T = (\text{Tmp} - 60)/33$$

$$P = (\text{Prs} - 27.5)/22.5$$

$$C = (\text{Cat Conc} - 0.0028)/0.0022$$

$$\text{SIV} = (\text{IV} - 115.28)/2.386 \quad \text{for 114 IV target}$$

$$\text{SIV} = (\text{IV} - 64.81)/4.2438 \quad \text{for 66 IV target}$$

Comparison of the two rate equations, [1] and [2], for the different target IV's, indicates a similarity in the number of terms and the magnitude of the coefficients. Catalyst concentration effect differs the most, with the lower IV being more sensitive to concentration. The SIV terms for the rate equation (114 IV) reflect the variability in sampling and can best be considered as correction factors. Although all the parameters enhance the reaction rate when they are increased, the model coefficients quantify the relative change for each parameter. Hence, temperature is the largest contributor to rate and it increases nonlinearly.

Prediction of how the reaction rate is affected by the experimental conditions is useful in estimating what conditions would be best for oil hydrogenation. Values can be calculated easily on a hand-held calculator from the equations given above. Another way to view the models is to plot a series of response-surface graphs. Figure 1 is one such plot for oil hydrogenated to 118 IV with 0.002% Pd. The effects of varying pressure and temperature can be seen readily. For example, at low temperature and pressure, the reaction rate is about 0.2 IV/min, but raising the temperature and pressure can increase the rate to greater than 1.6 IV/min. For the IV drop here, this corresponds to an 83-min reaction time at the lower conditions versus just a 10-min reaction time at the upper conditions. Nickel catalysts have comparable rates only at temperatures greater than 140 C.

One advantage of the reaction rate models is that reasonable predictions can be made for the required amount of catalyst. For example, if a 30-min reaction time is desired and the reaction conditions have been chosen based on other factors, then the rate models can be used to calculate the minimum catalyst needed. Thus, for a reaction at 100 C and 40 psig pressure, the required catalyst level is 0.0015% Pd. Because catalyst concentration and batch time are primary controllable variables in per-batch cost, the overall economics of using palladium can be estimated.

Catalyst-Induced Isomerization

The degree of *trans*-isomer formation that occurs during reaction can have significant impact on the physical properties of the hydrogenated oil and must be considered when choosing reaction conditions. Models for *trans*-isomer content were developed for both IV regions (equations [3] and [4]).

$$\begin{aligned} \text{Trans (\%)} = & 23.7 + 1.54(T) - 1.11(P) - 4.69(C) \\ & + 1.04(T)(P) + 0.86(T)(C) \end{aligned}$$

$$(114 \text{ IV}) \quad R^2 = 0.968 \quad [3]$$

$$\text{Trans (\%)} = 51.69 - 3.49(P) - 3.14(C) - 2.31(T)(P) - 2.49(P)(C)$$

$$(66 \text{ IV}) \quad R^2 = 0.839 \quad [4]$$

Generally, the *trans*-isomer content resulting from the use of palladium catalyst is higher than that resulting from the use of nickel catalysts. For the salad oil (114 IV range), the *trans*-isomers varied from 15 to 30% for palladium catalysts, with most values >20%. The high *trans*-isomer content would be expected to raise the stearin losses during winterization. This is undesirable and thus would limit the use of palladium for salad oil production.

Conversely, in shortening basestocks, the degree of *trans*-isomerization is an important factor in the melting characteristics. Figure 2 compares the *trans*-isomer content at two different IV's for the 10 batches. At the lower IV, the *trans*-isomer content is nearly the same as that obtained with nickel catalysts. However, the ability to modify the *trans*-isomer content is quite limited; the reaction conditions have only minor effects on the *trans*-isomer content. Low temperatures yield reasonable *trans*-isomer content but require high pressure and high catalyst concentrations that greatly add to the cost of operation.

Catalyst Selectivity

Catalyst selectivity is also an important consideration for vegetable oil hydrogenations. The literature contains some conflicting information on palladium selectivity, which probably is due to the reaction conditions employed. In the present study, reasonable models were obtained based on experimental data for both triene and diene selectivity.

$$\begin{aligned} \text{Triene Selectivity} = & 2.32 - 0.11(\text{SIV}) - 0.43(\text{SIV})^2 - 0.17(T) \\ & + 0.31(P) + 0.10(C) + 0.21(T)(P) \\ & + 0.23(T)(C) + 0.22(P)(C) \end{aligned}$$

$$(114 \text{ IV}) \quad R^2 = 0.999 \quad [5]$$

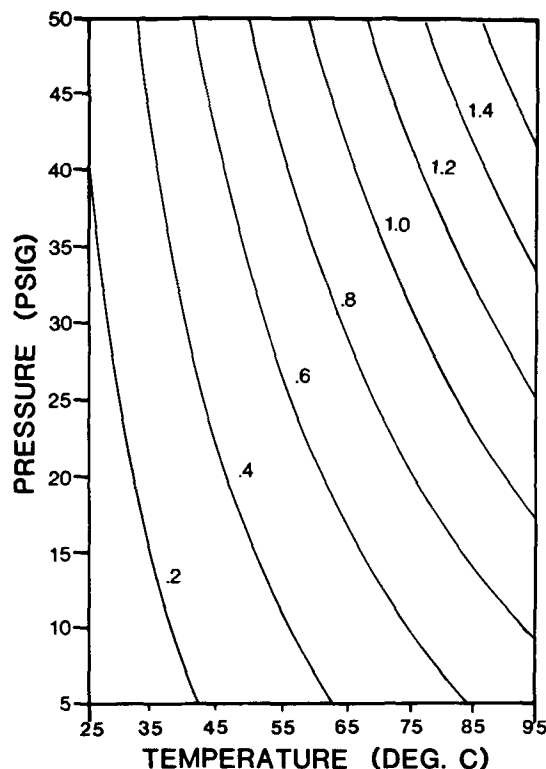


FIG. 1. Effect of pressure and temperature on reaction rate (IV/min) to 116 IV for 0.0020% Pd.

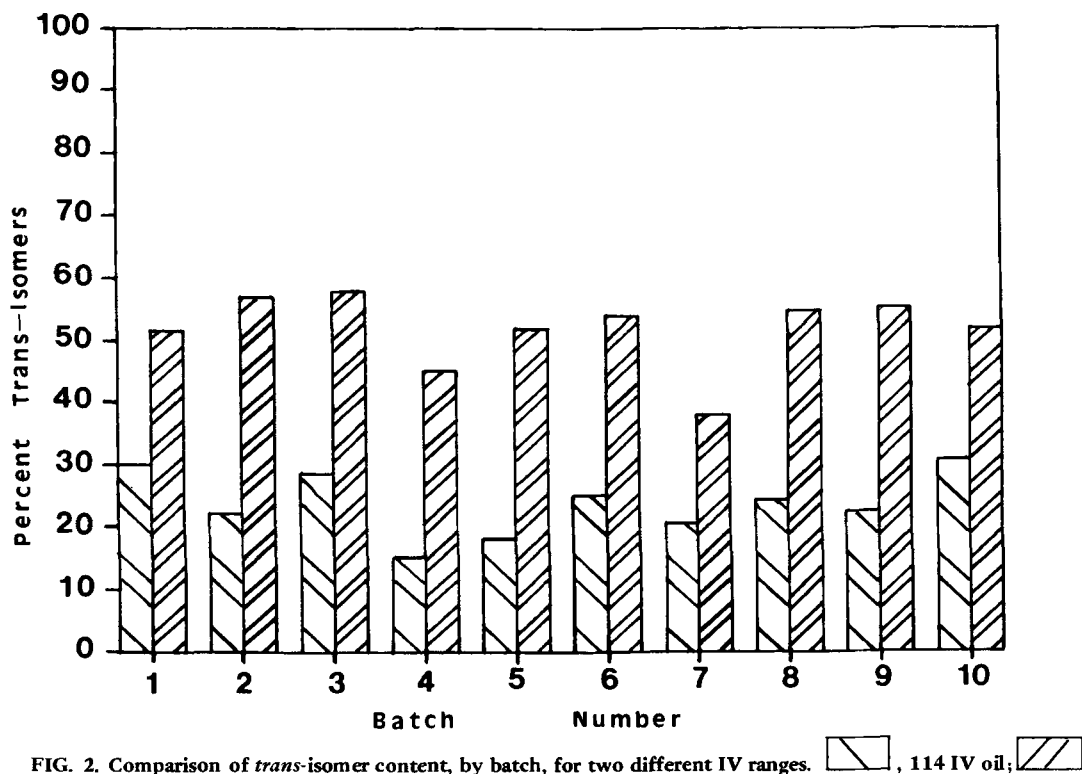


FIG. 2. Comparison of *trans*-isomer content, by batch, for two different IV ranges. , 114 IV oil; , 66 IV oil.

$$\text{Triene Selectivity} = 0.650 - 0.114(\text{SIV}) - 0.181(\text{T}) - 0.197(\text{C})$$

$$- 0.107(\text{T})(\text{P}) + 0.184(\text{T})(\text{C})$$

$$(66 \text{ IV}) \quad R^2 = 0.963 \quad [6]$$

$$\text{Diene Selectivity} = 11.67 + 1.64(\text{T}) - 1.39(\text{P}) - 4.76(\text{C})$$

$$(114 \text{ IV}) \quad R^2 = 0.804 \quad [7]$$

$$\text{Diene Selectivity} = 31.71 - 7.21(\text{P}) - 17.71(\text{T})(\text{C})$$

$$(66 \text{ IV}) \quad R^2 = 0.710 \quad [8]$$

Fatty acid composition data were used to calculate selectivity using the computer program given in the AOCS Standard Activity Method (5). A response-surface plot based on the model for linolenic selectivity (Fig. 3) shows the trend for oil hydrogenated to 116 IV. Temperature has a significant effect on selectivity, with the best selectivity being at low temperature. Increasing pressure generally has a positive effect on selectivity, the change in selectivity being more pronounced at higher temperature. In general, palladium is capable of about the same range of linolenic selectivity as nickel catalysts, but at lower temperatures and at lower metal concentration.

Linoleate selectivity follows a different relationship, as illustrated in Figure 4. For larger IV drops, the best diene selectivity is at high temperature (93 C) and low pressure. Even then, only moderate selectivity is obtained. Typically, palladium shows a range of selectivity similar to that of nickel catalysts and should be able to make nearly the same hydrogenated oil products when similar *trans*-isomer contents are obtained.

Both *trans*-isomer content and selectivity are important in determining the fat characteristics of hydrogenated soybean oil. Some solid-fat indexes illustrating this with

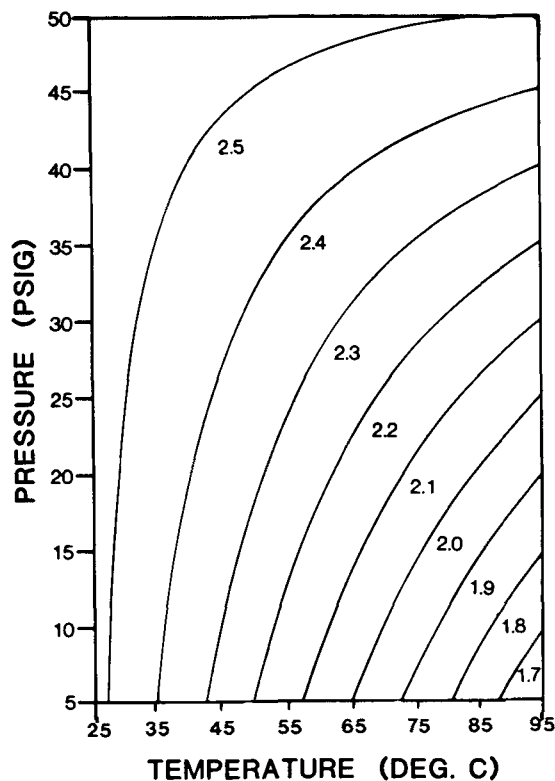


FIG. 3. Effect of pressure and temperature on linolenate selectivity (116 IV, 0.0020% Pd).

palladium data are compared to an approximate range for a margarine basestock in Figure 5. The two curves plotted for palladium show the changes in selectivity observed for the conditions of this study. The shape of the curves indicates that a basestock could be made at a slightly higher IV than

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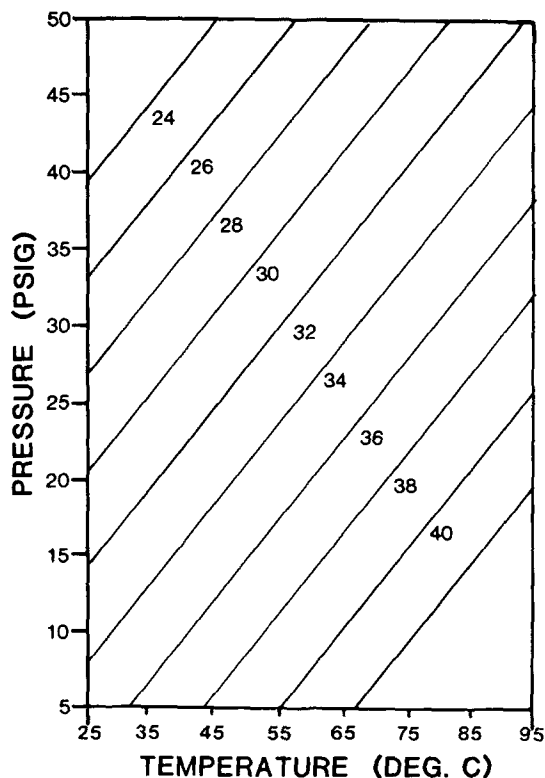


FIG. 4. Effect of pressure and temperature on linoleate selectivity (116 IV, 0.0020% Pd).

those of the examples. Additionally, the *trans*-isomer content does not differ much for the two samples. Based on the models, it appears that a margarine stock could be made at 66 to 68 IV. This is consistent with the conclusion of Zajcew (7), who studied palladium hydrogenation of various oils at higher pressures.

The method described here for evaluation of catalyst performance has several clear advantages over other procedures, including the AOCS Standard Activity Method (5). It is possible, using the models and response-surface plots, to pick the range of reaction conditions that best makes the desired oil product. Usually that involves balancing the amount of catalyst, reaction time, *trans*-isomer content and catalyst selectivity. Because the cost of palladium is quite high, it is important to reduce catalyst usage to only that needed to achieve the minimum acceptable reaction rate. The effective cost of catalyst, even with palladium recycling, is still more than 10 times the cost of nickel catalysts. The extreme activity of palladium and credits for recycling catalyst offset some of the cost difference. Since it is possible to use palladium for a range of oil products similar to that obtained using nickel catalysts, the economics of palladium usage become heavily dependent on the catalyst reusability. In separate experiments, from three to five reuses were possible without significant decrease in catalyst activity. This may mean that it is both feasible and

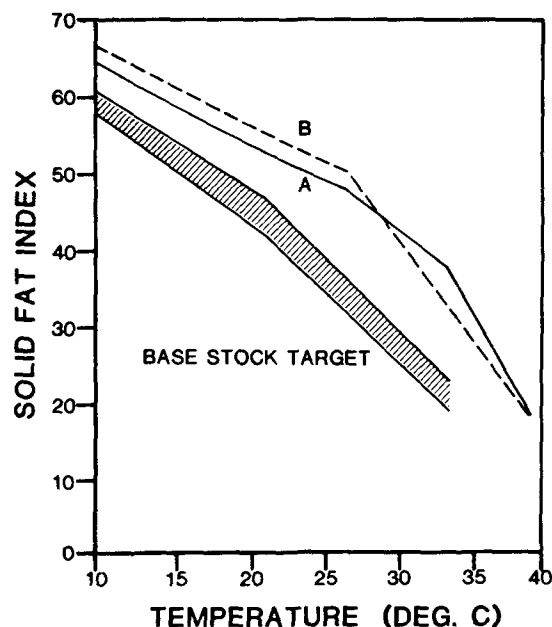


FIG. 5. Solid Fat Index for two different batches. Batch A is for high selectivity (64.4 IV, 52% *trans* isomers), Batch B for low selectivity (65.1 IV, 54% *trans* isomers). Basestock target suggested from the literature (8).

possible to use palladium economically for hydrogenation of soybean oil to a variety of products.

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