

A STATISTICAL EVALUATION OF THE EFFECTS OF PROCESS VARIABLES DURING CATALYTIC HYDROGENATION OF PASSION FRUIT (*passiflora edulis*) SEED OIL

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Abstract - Hydrogenation of passion fruit (*passiflora edulis*) seed oil was carried out with a commercial nickel/silica catalyst under different experimental conditions. The influence of reaction parameters (reaction temperature, hydrogen pressure, amount of catalyst, agitation rate and reaction time) on the response variable (iodine value) was studied using a central composite rotatable design and six center points for replication. Under the experimental conditions used, the model response equations for the iodine value showed good agreement with the experimental results.

Keywords: Vegetable oil, hydrogenation, catalyst, factorial design.

INTRODUCTION

Hydrogenation of vegetable oils is an important practice in the modification of fats and oils. Three-phase chemical reactions involving solid catalysts and liquid and gaseous reactants are commonly encountered in the chemical industry. Efficient gas transfer to a liquid phase and good mixing near the catalyst particle are in many cases essential to the success of the process occurring only when the liquid vegetable oil, hydrogen gas and solid catalyst are brought together under the correct set of conditions, due to low solubility of a gaseous reactant in the liquid phase (Choi et al., 1986; Allen, 1981).

In today's world of increasing population and limited resources, hydrogenation processes play a vital role in improving both the quality and quantity of food products (Puri, 1980). The composition and properties of the final product depend on various operating factors, including catalyst type and concentration, agitation rate, hydrogen pressure and temperature. Among these factors, the most important is the type of

catalyst. Currently, the most widely used commercial catalyst for edible oil hydrogenation is active nickel supported on an inert substance (Chu and Lin, 1991).

Despite the fact that several hydrogenation processes of vegetable oils have been studied since 1970, when Allen and Covey reported on the effects of process variables on the formation of trans-unsaturation during vegetable oil hydrogenation (Allen and Covey, 1970), to the best of our knowledge, no such study has reported on passion fruit seed oil, using the factorial experimental design.

The passion fruit is a widely known species, largely cultivated extensively in the state of Pará. Crops are abundant and the fruit is consumed and industrialized by a local industry making the production of juice a commercial and profitable endeavor. This activity produces lots of seeds which are considered subproducts and have not been utilized to date. The catalytic hydrocracking of vegetable oils has also been studied using this species and other native ones cultivated in the Amazon region (Da Rocha Filho et al., 1992, 1993). These studies aimed at increasing the aggregate values of the oils.

Thus, the present study was conducted to show that statistical methods allow us to obtain a useful model for controlling reactions parameters with a reduction of cost and number of experiments as well.

The experimental study, which used a central composite rotatable design (Box et al., 1978), was undertaken in order to establish the relationship of the iodine value as a of mathematical function of the reaction temperature, hydrogen pressure, amount of catalyst, agitation rate and reaction time.

From preliminary trials, appropriate values for five levels of the factors (reaction temperature, hydrogen pressure, amount of catalyst, agitation rate and reaction time) were selected to carry out the final experiments (Ramirez et al., 1994). The results from these final experiments were used to build a statistical model which uses coded values (-2, -1, 0, +1, +2) for the experimental parameters. In this statistical model, the real influence of each factor is calculated without being affected by its relative magnitude in relation to the magnitude of the other factors. Finally, the statistical model must be transformed into an experimental model, which uses real values of the different parameters expressed in their normal units.

MATERIALS AND METHODS

Materials

Passion fruit (*passiflora edulis*) seeds were purchased from a local juice industry (AMAFRUTA S.A). These seeds are useless in the juicemaking process. The seed oil extraction was carried out in a soxhlet extractor using n-hexane solvent with a 27% yield of dry material, resulting in a fatty acid methyl ester composition of 10% palmitic acid (16:0), 2.25% stearic acid (18:0), 19.63% oleic acid (18:1) and 68% linoleic acid (18:2), measured by gas chromatography (GC) with methyl heptadecanoate as an

internal standard. The commercial nickel/silica catalyst used in this experiment was Pricat 9912 (Unichema Chemie GmbH, Emmerich, Germany).

Hydrogenation

The hydrogenation process was carried out in a $2.5 \times 10^{-3} \text{ m}^3$ Parr pressure reactor, model 4576. After the introduction of 0.1kg of passion fruit seed oil and a certain amount of catalyst ([Table 1](#)), the reactor was sealed. When the oil/catalyst slurry reached the desired temperature, hydrogen was introduced into the system. This moment was considered to be the initial point of the reaction. At the end of the hydrogenation process, the product was filtered in a vacuum system.

Analysis

The hydrogenation was monitored by measuring the iodine value, according to standard AOCS (Official Methods, Cd 1-25, 1973).

Experimental Design

Experimental designs are frequently used to obtain empirical relationships based on a mathematical model between one or more of the measured responses and a certain number of factors. It was assumed that the hydrogenation reaction would be affected by five independent ξ_i variables (reaction temperature, ξ_1 ; hydrogen pressure, ξ_2 ; amount of catalyst, ξ_3 ; agitation rate, ξ_4 ; and reaction time, ξ_5). In addition, it was assumed that one dependent variable (referred to as a response), η (iodine value), which was experimentally measured, also defined the system.

$$\eta = f(\xi_1, \xi_2, \xi_3, \xi_4, \xi_5) \quad (1)$$

Second degree polynomial equations were assumed to approximate the true functions:

$$\eta = \beta_0 + \sum_{i=1}^5 \beta_i x_i + \sum_{i=1}^5 \beta_{ii} x_i^2 + \sum_{i=1}^4 \sum_{j=i+1}^5 \beta_{ij} x_i x_j \quad (2)$$

where β_0 , β_i , β_{ii} and β_{ij} are regression coefficients and ξ_i are the coded independent variables linearly related to ξ_i . The coding of ξ_i into x_i is expressed by the following equation:

$$x_i = \frac{\xi_i - \xi_i^*}{d_i} \quad (3)$$

where ξ_i is the real value in original units, ξ_i^* the real central value in original units, and d_i the absolute difference between ξ_i and ξ_i^* .

The statistical design chosen for this study was a central composite rotatable design with five variables. The range and center point of the five variables (Chung et al., 1996) were chosen based on preliminary trials ([Table 1](#)). For the five variables, this design yielded 48 experiments with thirty-two (2^5) factorial points, ten extra points (star points) to form a central composite design with $\alpha = 2$, where α is the distance from the center

point of the design to a star point or a star arm, and six center points for replication. All the experimental runs were performed at random (Table 2).

The planning matrix and regression multiple as well as other analysis, variance and canonical, were carried out with the aid of statistical software Statgraphics version 7.0, a statistical graphics system by Statistical Graphics Corporation.

Table 1: Coded Levels for Independent Variables Used in Developing Experimental Data.

Variable	Coded level				
	-2	-1	0	+1	+2
T(K)	443.15	453.15	463.15	473.15	483.15
$P \cdot 10^{-5}$ (N/m ²)	20	23	26	29	32
*C(%)	0.11	0.22	0.33	0.44	0.55
A(rpm)	200	337.5	475	612.5	750
t(s)	3600	4800	6000	7200	8400

* amount of catalyst as percent nickel.

RESULTS AND DISCUSSION

The second degree polynomial which relates the iodine value and the hydrogenation conditions is:

$$Y = 45.5198 + 1.3165X_1 + 2.6850X_2 + 1.0135X_3 + 0.6030X_4 + 0.9235X_5 - 0.8575X_1X_4 + 0.6394X_1X_5 + 0.5650X_2X_4 - 0.5787X_3X_4 - 0.5789X_3^2 - 0.5714X_5^2 \quad (4)$$

The coefficient of determination for this model was $R^2 = 0.7679$ with a lack of fit greater than 5%.

A second-order model with the characteristics of equation (4) could be rewritten in canonical form in such a way that its fundamental nature is clearly revealed.

Canonical analysis consists of (4) shifting the origin to a new point S (stationary) and rotating the axes so that they correspond to the new origin labeled W_i , as show in the equation (5).

Thus, the equation (4) becomes:

$$Y - Y_S = \lambda_1 W_1^2 + \lambda_2 W_2^2 + \lambda_3 W_3^2 + \lambda_4 W_4^2 + \lambda_5 W_5^2 \quad (5)$$

where Y and Y_S are real values at any point and at a new point S (stationary), respectively; λ_i are constant (eigenvalue); and W_i are the independent variables in the canonical form.

In this work, the canonical form is represented by equation (6) and the linear relationship of the coordinates by equations (7a) to (7e).

$$Y - 45.5198 = 0.0515W_1^2 - 0.2841W_2^2 - 0.6648W_3^2 - 0.8347W_4^2 + 0.5819W_5^2 \quad (6)$$

$$W_1 = -0.5402X_1 - 0.7790X_2 + 0.0652X_3 - 0.1419X_4 - 0.2773X_5 \quad (7a)$$

$$W_2 = -0.3368X_1 + 0.4998X_2 + 0.4935X_3 - 0.5027X_4 - 0.3748X_5 \quad (7b)$$

$$W_3 = 0.1993X_1 + 0.0846X_2 - 0.6701X_3 - 0.1991X_4 - 0.6815X_5 \quad (7c)$$

$$W_4 = 0.4441X_1 - 0.1565X_2 + 0.5232X_3 + 0.4625X_4 - 0.5392X_5 \quad (7d)$$

$$W_5 = 0.5982X_1 - 0.3341X_2 + 0.1716X_3 - 0.6882X_4 - 0.1658X_5 \quad (7e)$$

The canonical analysis allows the best comprehension of the system, considering that in equation (4) the effects of the independent variables could not be interpreted singularly.

The stationary point, $S = X_{iS}$, could be inside or near the experimental region studied; in this case, the original coordinates are shifted to the origin. On the other hand, if the stationary point is far from the system studied, the original axes are not shifted (Akhazarova and Kafarov, 1982), as in this study.

The sign and magnitude of constant λ_i offer interpretations of the nature of the surface and stationary point.

This study presents λ_i with different signs correlated with correspondent variables (a $\lambda > 0$ minimum and a $\lambda < 0$ maximum), that shows a minimax (saddle or col). This type of occurrence in practice implies the existence of a system with several peaks, that is, several maximums at difference points. At another point, the magnitude of λ_i could offer important information on the system. It can be noted that the sensitivity of the system is affected by $|\lambda_i|$, such that the contribution of the independent variables is more important for greater absolute values (Myers, 1971 and Khuri & Cornell, 1987).

The significant lack of fit of the second-order model leads us to use a special cubic model, with a greater coefficient of determination that better represents the system.

Table 2: Experimental Data for Yield of Iodine Value

Run	Order in which runs were performed	x ₁	x ₂	x ₃	x ₄	x ₅	*Yield (iodine value)
Crude oil							141.05
1	15	-1	-1	-1	-1	-1	36.75
2	17	+1	-1	-1	-1	-1	43.32
3	48	-1	+1	-1	-1	-1	39.86
4	46	+1	+1	-1	-1	-1	40.31
5	40	-1	-1	+1	-1	-1	38.92
6	1	+1	-1	+1	-1	-1	43.55
7	18	-1	+1	+1	-1	-1	47.31
8	26	+1	+1	+1	-1	-1	49.22
9	28	-1	-1	-1	+1	-1	41.26
10	27	+1	-1	-1	+1	-1	41.65
11	44	-1	+1	-1	+1	-1	45.10
12	21	+1	+1	-1	+1	-1	46.70
13	47	-1	-1	+1	+1	-1	42.38
14	43	+1	-1	+1	+1	-1	41.40
15	32	-1	+1	+1	+1	-1	46.64
16	36	+1	+1	+1	+1	-1	47.89
17	19	-1	-1	-1	-1	+1	38.10
18	41	+1	-1	-1	-1	+1	41.42
19	39	-1	+1	-1	-1	+1	44.44
20	7	+1	+1	-1	-1	+1	49.38
21	5	-1	-1	+1	-1	+1	40.08
22	2	+1	-1	+1	-1	+1	49.50
23	37	-1	+1	+1	-1	+1	42.38
24	34	+1	+1	+1	-1	+1	50.91
25	16	-1	-1	-1	+1	+1	39.19
26	29	+1	-1	-1	+1	+1	44.76
27	13	-1	+1	-1	+1	+1	46.45
28	25	+1	+1	-1	+1	+1	52.13
29	22	-1	-1	+1	+1	+1	42.59
30	33	+1	-1	+1	+1	+1	43.77
31	20	-1	+1	+1	+1	+1	52.35
32	42	+1	+1	+1	+1	+1	49.99
33	14	-2	0	0	0	0	46.11
34	35	+2	0	0	0	0	46.39
35	3	0	-2	0	0	0	39.91
36	4	0	+2	0	0	0	52.40
37	31	0	0	-2	0	0	42.60
38	11	0	0	+2	0	0	43.84
39	24	0	0	0	-2	0	45.75
40	38	0	0	0	+2	0	43.41

41	12	0	0	0	0	-2	42.81
42	6	0	0	0	0	+2	43.69
43	8	0	0	0	0	0	46.08
44	45	0	0	0	0	0	44.50
45	10	0	0	0	0	0	47.47
46	9	0	0	0	0	0	43.64
47	23	0	0	0	0	0	46.40
48	30	0	0	0	0	0	44.24

* Reaction yield as iodine value (cg/g) difference between crude and hydrogenated oil.

$$\begin{aligned}
Y = & 45.5198 + 1.3165X_1 + 2.6850X_2 + \\
& + 1.0135X_3 + 0.6030X_4 + 0.9235X_5 - \\
& - 0.8575X_1X_4 + 0.6394X_1X_5 + 0.5650X_2X_4 - (8) \\
& - 0.5787X_3X_4 - 0.5789X_3^2 - 0.5714X_5^2 - \\
& - 0.7300X_1X_3X_4 - 0.7831X_2X_3X_5
\end{aligned}$$

The comparison of the experimental and calculated responses for the model (Figure 1), show the agreement between the observed and predicted values. From this figure, it is possible to see that the mathematical model used for the prediction of the response provides good agreement for the experimental data.

It is interesting to notice that the random distribution of the residuals (Figure 2) shows the absence of a trend which also indicates that the mathematical model is adequate since it does not detect any inconsistency between experimental and calculated values.

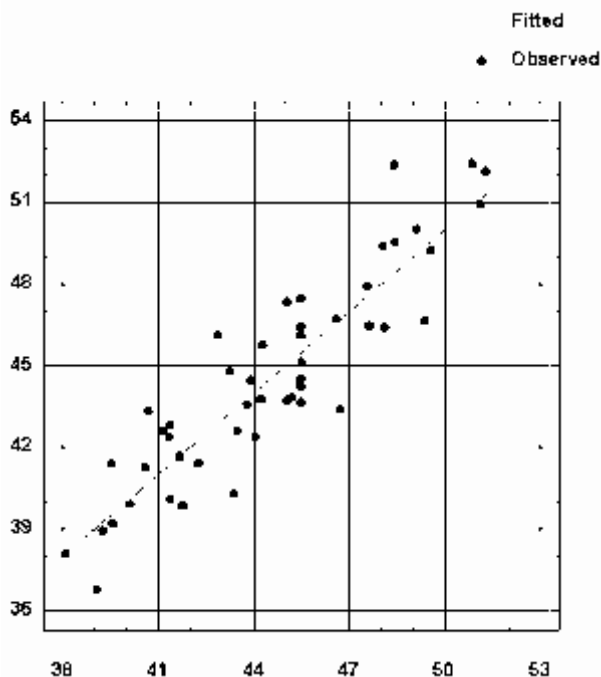


Figure 1: Comparison of the proposed model with the experimental results.

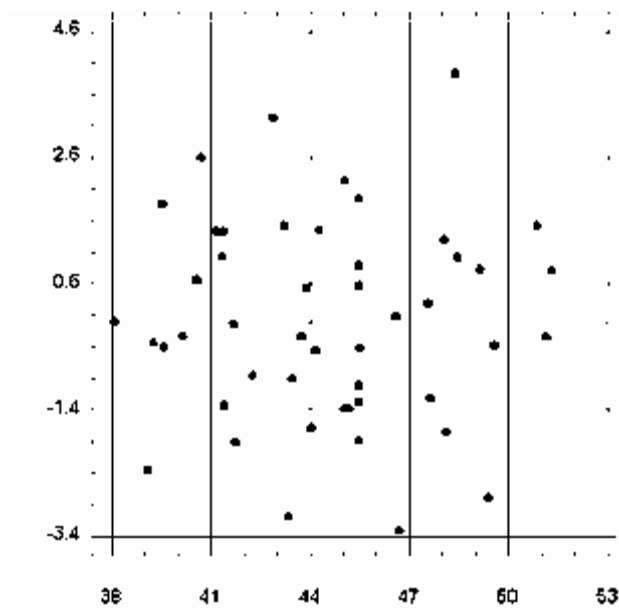


Figure 2: Distribution of the residual values.

It must be emphasized, that equation (8) is an empirical equation that describes the relation between the iodine value and the reaction conditions in our experimental reactor. This equation cannot be used to predict the iodine value in another reactor since agitation would probably be different, even if the same rpm agitator were used. This would result in a difference in the reaction. Clearly, the limitations in the use of the proposed model are those inherent in the statistical approach used here.

[Tables 3](#) and [4](#) show the calculated values of the coefficients, as well as their standard errors and corresponding significance levels and lower and upper limits.

In analyzing the results of the analysis of variance ([Table 5](#)), it can be observed that the regression is consistent ($R^2=0.821641$), suggesting that the coefficients or parameters as well as the model proposed describes quite well the relationship between the variables.

Table 3: Model fitting for results of the multiple regression of the statistical design of the experiment

Independent variable	coefficient	Std. error	t-value	Sig.level
AVERAGE	45.519773	0.494209	92.1064	0.0000
T	1.3165	0.299258	4.3992	0.0001
P	2.685	0.299258	8.9722	0.0000
C	1.0135	0.299258	3.3867	0.0018
A	0.603	0.299258	2.0150	0.0519
t	0.9235	0.299258	3.0860	0.0040
T.A	-0.8575	0.334581	-2.5629	0.0150
T.t	0.639375	0.334581	1.9110	0.0645

P.A	0.565	0.334581	1.6887	0.1004
C.A	-0.57875	0.334581	-1.7298	0.0927
C ²	-0.578864	0.342101	-1.6921	0.0998
t ²	-0.571364	0.342101	-1.6702	0.1041
T.C.A	-0.73	0.334581	-2.1818	0.0361
P.C.t	-0.783125	0.334581	-2.3406	0.0253

R-SQ. (ADJ.) = 0.7534 SE=1.892675 MAE=1.292566 DurbWat=2.633
48 observations fitted, forecast(s) computed for 0 missing val. of dep. var.

Table 4: 95 Percent confidence intervals for coefficient estimates

	Estimate	Standard error	Lower limit	Upper limit
AVERAGE	45.5198	0.49421	44.5152	46.5244
T	1.31650	0.29926	0.70819	1.92481
P	2.68500	0.29926	2.07669	3.29331
C	1.01350	0.29926	0.40519	1.62181
A	0.60300	0.29926	-0.00531	1.21131
t	0.92350	0.29926	0.31519	1.53181
T.A	-0.85750	0.33458	-1.53761	-0.17739
T.t	0.63937	0.33458	-0.04073	1.31948
P.A	0.56500	0.33458	-0.11511	1.24511
C.A	-0.57875	0.33458	-1.25886	0.10136
C ²	-0.57886	0.34210	-1.27426	0.11653
t ²	-0.57136	0.34210	-1.26676	0.12403
T.C.A	-0.73000	0.33458	-1.41011	-0.04989
P.C.t	-0.78312	0.33458	-1.46323	-0.10302

Table 5: Analysis of Variance (ANOVA) for the Full Regression

Source	Sum of squares	DF	Mean square	F-ratio	P-value
Model	561.070	13	43.1592	12.0482	.0000
Error	121.795	34	3.58222		
Total (Corr.)	682.865	47			

R-squared = 0.821641

Std. error of est. = 1.89268

R-squared (Adj. for d.f.) = 0.753444

Durbin-Watson statistic = 2.63259

Thus, the factors that affect the iodine value are in decreasing order A>C>t>P>T. The significant agitation rate was anticipated due to the fact that the main function of this parameter is to supply dissolved hydrogen to the catalyst surface. This reflects a

considerable interdependence between the response variable and the mass transference phenomena of the gas and liquid to and from the solid catalyst surface (Grau et al., 1988; Ariaansz and Meern, 1992), while the amount of catalyst and reaction time had less influence. However, this influence is still of remarkable importance since the activity of a catalyst depends on the number of active sites available for hydrogenation. These active sites may be located on the surface of the catalyst or deep inside the pores. It is thus evident that the transportation of the unsaturated fat and hydrogen will not be as free to the active sites in the pores as it is to the outer catalyst surface (Velasco et al., 1992; Klimmek, 1984; Dafler, 1977), which makes the reaction possible. In general, the elevation of hydrogen pressure and temperature causes the production of highly saturated material, which is normally obtained when large quantities of hydrogen are used (H_2), and a decrease in activation energy, resulting in an increase in the reactivity.

CONCLUSIONS

From the results of this study, the following conclusions can be drawn:

1. The proposed statistical model can predict the response, the iodine value, with reasonable accuracy within the range of the experimental conditions used in this study.
2. A study of the factors which affect the response shows agitation rate to be the most important.
3. The agitation rate was shown to have significant effects on the iodine value, not only by itself but also together with other independent variables (T, P and C), that is, in interaction with two and three variables.

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 hydrogenation in small equipment.

NOMENCLATURE

α Distance from the center point of the design to a star point or a star arm

GC Gas chromatography

AOCS American Oil Chemistry Society

ξ_i Independent variables

η Dependent variable

R^2 Coefficient of determination

ANOVA Analysis of variance

A Agitation rate

C Amount of catalyst

P Hydrogen pressure

T Reaction temperature

T Reaction time

TA Interaction with reaction temperature (T) and agitation rate (A)

TCA Interaction with reaction temperature (T), amount of catalyst (C) and agitation rate
PCt Interaction with hydrogen pressure, amount of catalyst (C) and reaction time
t-value Student' s t-test value
DF Degree of freedom
F-value Fisher' s test value
P-value Probability value

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