Computation of Nickel Catalyst Activity in the Hydrogenation of Triacylglycerol Oils

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ABSTRACT

The development of a new method for a faster and more accurate computation of the nickel catalyst activity was studied. This catalyst is used in partial catalytic hydrogenation of vegetable oils for production of edible fats. In order to index the activity, a computer program, CATACT, was developed using FORTRAN language. This program uses 3 easily determined experimental values as input data (refractive index at 60 C, catalyst concentration and hydrogenation time). Output data are catalyst activity indexes either in word or numerical form. The hydrogenation data were gathered from a laboratory reactor under laboratory conditions. Using these data, we computed the activity of Ni catalysts which have been reused in oil hydrogenation under industrial conditions. The classical method of determining such activity by evaluating the melting point is, in view of the very low activity of such catalysts, inadequate to provide sufficient information for easy interpretation.

INTRODUCTION

In addition to measuring technological conditions such as effectiveness of the prerefining process, temperature, pressure and mixing efficiency, the process of partial catalytic hydrogenation (PCH) is determined by the properties of the catalyst itself, the most important being selectivity and activity. The composition and properties of the final product are dependent on the accuracy, speed and reproducibility of determinations of these catalyst parameters along with the other PCH conditions; PCH control is therefore aimed at obtaining the predetermined properties. Expression of catalyst selectivity is possible and satisfactorily accurate using nomograms (1-3) or computers (4).

Catalyst activity is determined by the usual methods (5,6) and is expressed as the value of the melting point (mp) at which rapeseed oil solidifies in 60 min under laboratory and standard conditions regulating the reactor, stirrer revolutions, amount of hydrogen, temperature and quantity of catalyst. Hydrogenation proceeds with 0.2 % Ni present in the oil.

The activity of fresh catalyst is high, which is marked by a considerable rise in the mp of standard rapeseed oil after use in hydrogenation.

On the other hand, a catalyst which has already been used in oil hydrogenation shows poor activity with less rise in the mp of standard rapeseed oil after use in hydrogenation. At room temperature (20 C), the melting points cannot be determined.

Nickel catalysts are sometimes reused several times in the hydrogenation of triacylglycerol oils in industry. This means that ca. 90% of all hydrogenation processes are done with a spent catalyst (7). Besides the increased poison evolved through repeated use of these catalysts, they lose their activity as they become fatigued. The mp of standard rapeseed oil cannot be determined after the hydrogenation with such catalysts and use of the classical method for determining activity of an industrial catalyst is therefore impossible.

The mp of standard rapeseed oil can be determined with the usual method using higher weights of industrial catalysts. With catalysts of low activity, it is impossible to determine the true mp because of the small volume of laboratory hydrogenation reactors (300 ml).

The catalyst activity can be expressed as the mean rate at which the first 25% of the determined olefinic bonds become saturated with hydrogen using the number of normal ℓ H_2/hr/catalyst mass (pure nickel) (8) with respect to the change of iodine value over time (9).

It is simpler to express the activity as the difference in iodine value (IV) or as the drop in the refractive index (n_D^{60}) within a time unit.

Dafler (10) quickly and accurately determines catalyst activity by the graphic indexing method under fixed conditions of temperature, hydrogen pressure, mixing rate and catalyst concentration.

In this paper, the computer determination and indexing of catalyst activity within the entire range, using the FORTRAN-derived computer program CATACT, are described in detail.

EXPERIMENTAL PROCEDURES

Laboratory Hydrogenation Conditions

The hydrogenations were carried out in a 300-ml stainless steel hydrogenation reactor equipped with stirrer, thermometer and hydrogen inlet and outlet well, all as required by conditions given in references 5 and 6. In the standard laboratory hydrogenation process, sunflower oil of pharmaceutical purity was used as characterized by the following constants: saponification value (SV) = 185.4; IV = 130.4, n_D^{60} = 1.4615. Operational conditions were: temperature = 180 C; hydrogen flow rate = 30 ℓ/hr; weight of hydrogenated oil = 100 g; % Ni in fresh catalyst = 13.01; and stirrer revo-

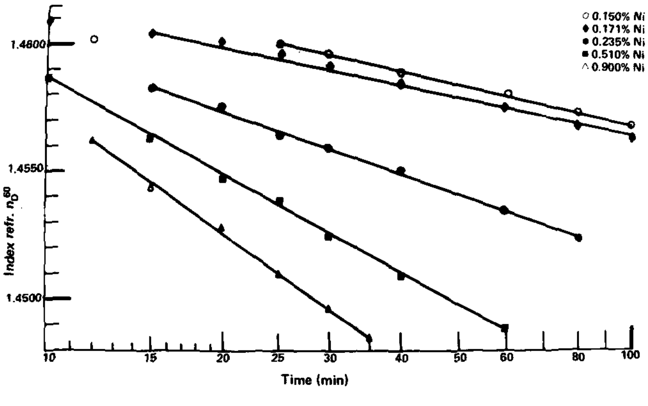

FIG. 1. Dependence courses of Ni concentration and the times for the 5 hydrogenations performed under standard laboratory conditions.

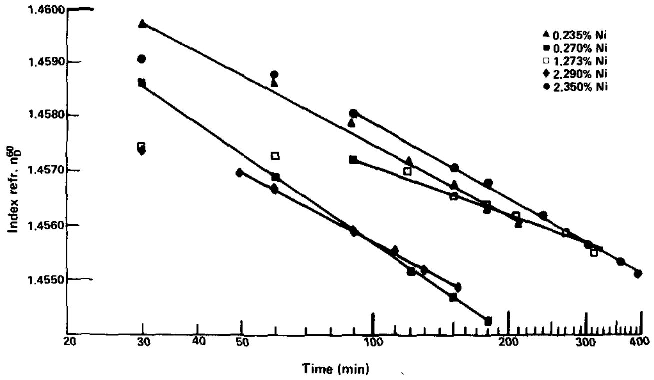

FIG. 2. Basic standard straight line satisfying Equation VI obtained after the approximation of the polynomial of a system of equations of straight line limit the zones of the catalysts concentrations with chosen expressions of catalysts activities.

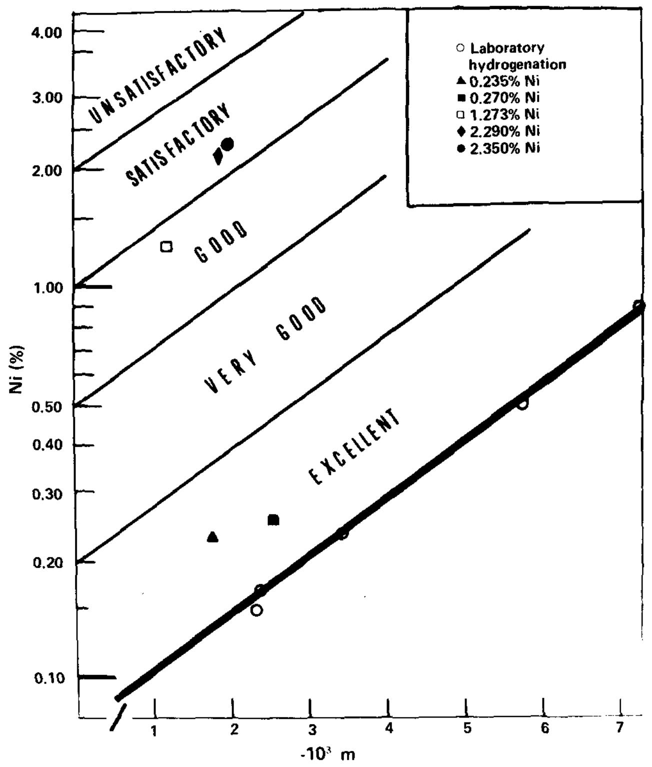

FIG. 3. Courses of the linear parts of the dependences of the % Ni and times for the 5 samples of sunflower oil hydrogenated under technological conditions similar to industrial situations.

lutions/minute = 2300. Under these conditions samples containing Ni in oil at 0.15, 0.17, 0.23, 0.51 and 0.90% were hydrogenated.

Industrial Hydrogenation Conditions

Preferred crude sunflower oil hydrogenated at the processing plant was selected and then observed for the industrial hydrogenation. Prerefined and vacuum-dried sunflower oil (5,000 kg) were mixed with (a) fresh and (b) used catalyst.

Following the repumping to the hydrogenation reactor (closed system), the mixture was heated to 110 C, the stirrer put into operation (840 rpm) and the hydrogen supply opened. Regular sample-taking included recording the hydrogenation time (min), temperature and pressure. Samples were taken from 5 PCH, the catalyst from them was filtered at 60 C and the water was removed simultaneously with anhydrous Na_2SO_4.

TABLE I

Output Over-all Chart of Printed Values (CATACT Computer Program): Industrial Hydrogenation of Sunflower Oil

Hydrogenation time (min)		Refractive index Measured	Refractive index Linearized
TAU[a]	LN TAU	N_D^{60+}	N_D^{60}-Computed
90	4.49981	1.45720	1.45720
120	4.78749	1.45700	1.45686
150	5.01064	1.45670	1.45660
180	5.19296	1.45640	1.45639
210	5.34711	1.45620	1.45621
270	5.59842	1.45590	1.45591
315	5.75257	1.45550	1.45573

M = -0.00117; % Ni = 1.273; R = -0.98960; catalyst activity = very good: 4.00.

[a] Input data.

Determination of the Physicochemical Constants

In samples of fats hydrogenated in laboratory and industry the following physical and chemical constants were determined: IV, mp and solidification point (6). The refractive index was computed according to the Wattson-Soudborough equation (11) for vegetable oil:

$$n_D^{60} = 1.4468 + 1.03 \times 10^{-4} \times IV + 7.3 \times 10^{-8} \times IV^2 \quad [I]$$

The Ni content in the catalyst (% Ni) was determined by the titrimetric/chelatrometric method (12) which requires 2 hr for completion.

Computation of the Catalyst Activity

An analogous Dafler method was used to compute the catalyst activity. As a basis for obtaining fast, accurate analytical information the refractive index determined by the IV according to Equation I was used.

Dependence of n_D^{60} on the logarithm of hydrogenation time was tabulated and found to be approximately linear within most of the measurement range (a certain time after the start of the hydrogenation process). The regressions of linear parts of the curves representing the hydrogenation changes from the used catalyst offered a group of pseudorate equations of the form:

$$n_D^{60} = m \cdot (\ln\tau - \ln\tau_o) + n_{Do}^{60} \quad [II],$$

where τ is the complete hydrogenation time, τ_o is the hydrogenation time starting from which n_D^{60} dependence on τ is approximately linear, n_{Do}^{60} is the refractive index at $\tau = \tau_o$, m is the regression coefficient - total pseudo-rate constant.

It was assumed that given values n_D^{60} were measured at τ_i places where i = 1,2,.k. If we denote:

$$x_i = \ln\tau_i - \ln\tau_o \quad [III],$$

the regression coefficient-pseudo-rate constant m was determined so that:

$$m = \frac{\sum_{i=1}^{k} n_{D_i}^{60} \times x_i - n_{Do}^{60} \sum_{i=1}^{k} x_i}{\sum_{i=1}^{k} x_i^2} \quad [IV]$$

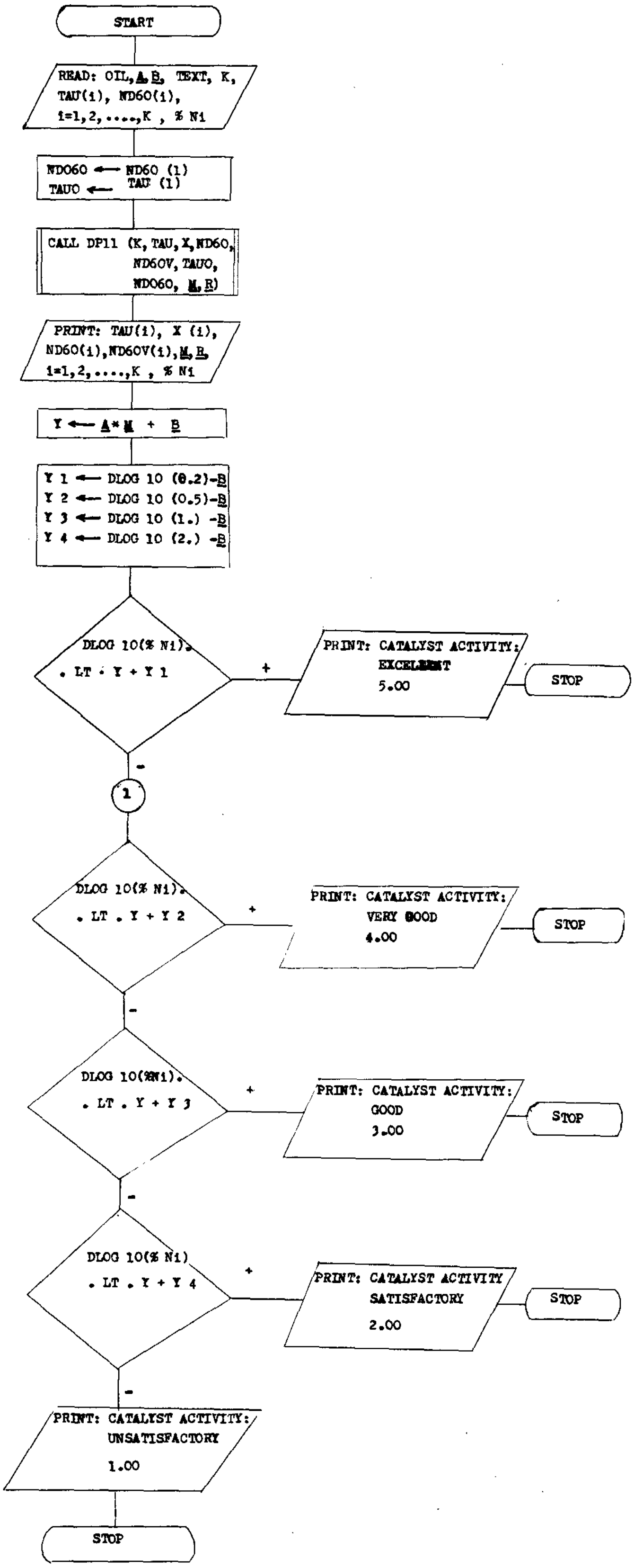

FIG. 4. Flow diagram of computing program CATACT for activity determination.

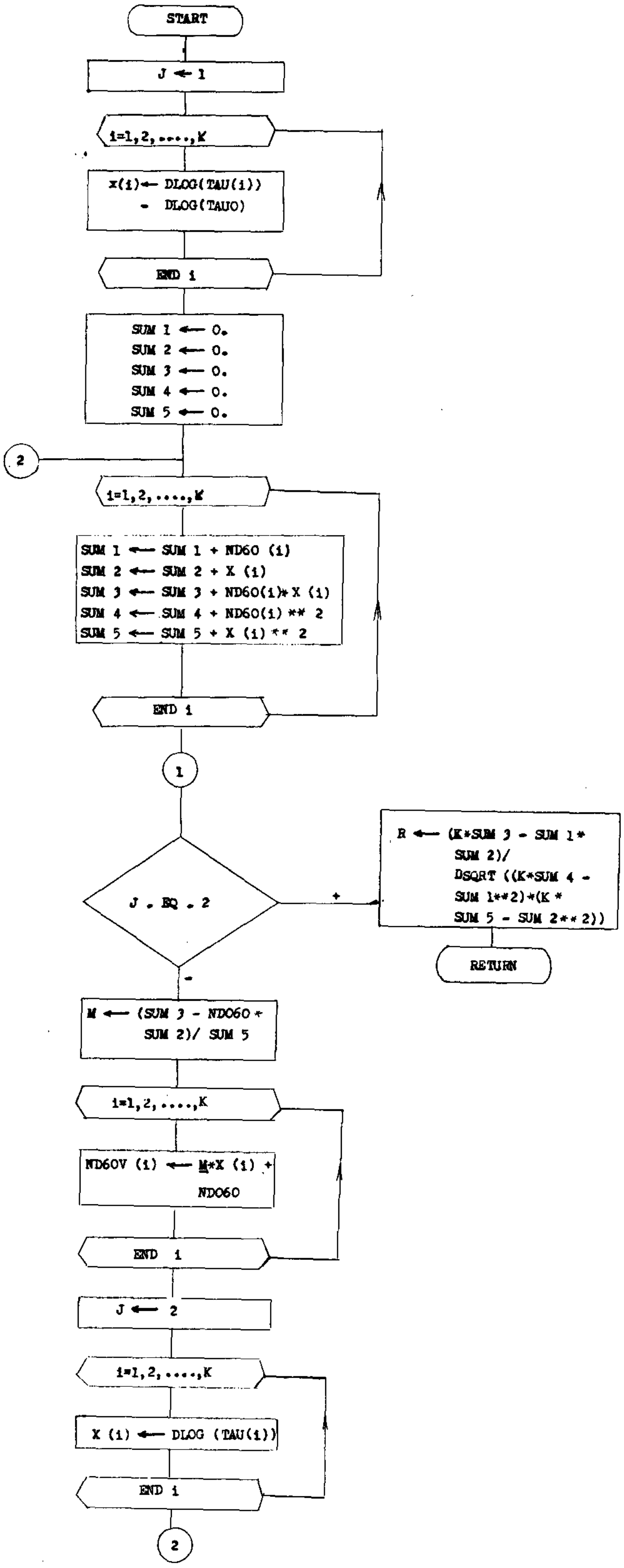

FIG. 5. Flow diagram of computing subprogram DP11 of program CATACT.

TABLE II

Characteristics of Ni Catalysts Computed by CATACT Program in Five Hydrogenations under Industrial Technological Conditions

Hydrogenation process number	% Ni	Pseudo-rate constant m	Correlation coefficient of linearity	Activity of used catalyst
1	0.235	-0.00170	-0.99505	Excellent 5
2	0.270	-0.00246	-0.99905	Excellent 5
3	1.273	-0.00117	-0.98960	Very good 4
4	2.290	-0.00184	-0.99922	Satisfactory 2
5	2.350	-0.00195	-0.99955	Satisfactory 2

The computing program for the catalyst activity indexing provided the solution in 4 subsequent stages using subprograms (a) for the determination of the regression coefficient-pseudo-rate constant m for standard samples of laboratory hydrogenations; (b) for the determination of the pseudo-rate constants m for nonstandard samples of industrial hydrogenations; (c) for the determination of the standard straight line; and (d) for the proper indexing of the used catalyst activity.

For evaluation of linearity the correlation coefficient of linearity r (13) was calculated.

According to probability theory the dependence of values of variable n_D^{60} on $\ln\tau$ is linear if the absolute value of the correlation coefficient r $(n_{D_1}^{60} \ln\tau)$ is very close to 1. The correlation coefficient was computed and linearity evaluated according to relationships given in reference 13.

To facilitate the determination of coefficient of the standard regression straight line, a graphical interpretation of the dependence formula % Ni = f (m) was developed, for which the logarithmic expression of an excellent linearity is:

$$\log \% \mathrm{Ni} = a \times m + b \qquad [V]$$

The values giving series of measurements which implemented conditions of linearity were analyzed using the polynomial regression analysis used in the first subprogram for the computation of the pseudo-rate constants m. For the calculation of the regression coefficients a and b of the straight line, a new subprogram was established using as input data the values of the previously computed pseudo-rate constants m and the corresponding concentration of the Ni catalyst.

Orders to the output print also include the simultaneous recording of the values of the coefficients a and b of the standard straight-line Equation V and the linearity r of the correlation coefficient. The straight line expressing the conditions and relationships between the laboratory hydrogenations was defined as the standard straight line representing 100% activity of the Ni catalyst.

Both the pseudo-rate constants m and correlation coefficients of the linearity r for the nonstandard industrial hydrogenations were calculated using an independent subprogram.

The pseudo-rate constants m obtained from the polynomial approximation analyses represent the quantitative basis for the expression of the catalyst observed in the industrial PCH.

The equidistant lengths of points of the dependences of log % Ni on m from the orthogonal of the standard straight line where used in the indexing of the catalyst activity. The concentrations of the catalysts within the predetermined ranges were taken as limits for the printing of the equidistances, these being expressed as: excellent, very good, good, satisfactory and unsatisfactory; or by their numerical equivalents: 5.00, 4.00, 3.00, 2.00 and 1.00.

RESULTS AND DISCUSSION

Using the refractive index, catalyst concentration and hydrogenation time, the values of which can be experimentally obtained easily and quickly, it was possible to determine the catalyst activity in full range by a computing method. The semilogarithmic interpretations of dependences of the Ni catalyst concentrations and of the time required for the 5 standard laboratory hydrogenations can be seen in Figure 1.

The equation of the standard straight line has been obtained from the polynomial regression analyses of linear parts of the straight line dependences between the laboratory hydrogenations:

$$\log \% \mathrm{Ni} = -149.53 \times m - 1.14 \qquad [VI],$$

with the coefficient of correlation r = 0.997. Its strictly linear course is seen in Figure 2. The parallels to the standard straight line in Figure 2 clearly limit the equidistant zones of the catalyst activity indices (these being printed in the CATACT computing program at the output in the corresponding alphanumerical expressions).

The semilogarithmic interpretations of the linear parts of the dependence between the Ni catalyst concentration and the time required for 5 experimentally measured industrial PCH are seen in Figure 3. From these interpretations, using the computing program CATACT, the value expressing the activity of the Ni catalyst used industrially in the PCH process (Table I) was calculated.

Table I and Figures 4 and 5 illustrate the overall chart of the output part of the CATACT computer program, i.e., the input data, preliminary calculations and final results obtained in the computation of the Ni catalyst activity. The characteristics of the Ni catalyst studied in 5 industrial PCH are tabulated (Table II).

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