Intrinsic Selectivities and Yields in the Catalytic Hydrogenation of Polyenoic Fatty Acid Methyl Esters

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Precise values of the intrinsic selectivities and yields for the hydrogenation products of methyl linolenate (Ln) and methyl linoleate (L) obtained under carefully controlled conditions using a commercial Ni catalyst are presented and analyzed in detail. The existence of a preferential adsorption of Ln and a significant co-hydrogenation of its double bonds are confirmed as being the dominant features under typical vegetable oil processing conditions.

It is shown that the values of the selectivities that are obtained from the classical consecutive reactions network account for the intrinsic selectivity of the catalyst only while hydrogenating feedstocks with moderate to low (<10%) contents of Ln.

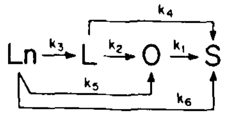
A diversity of conceptual descriptions regarding selectivity, usually based on simple kinetic schemes, has been put forward to describe the different relative reactivities of the unsaturated species normally found during vegetable oil hydrogenation processes (1-3). Usually, the preferential hydrogenations of linolenate respect linoleate, and linoleate respect oleate esters, are quantified with "selectivity ratios" calculated from the relationships SLn = k_3/k_2 and SL = k_2/k_1, respectively, in the consecutive reactions macromodel:

$$\mathrm{Ln} \xrightarrow{k_3} \mathrm{L} \xrightarrow{k_2} \mathrm{O} \xrightarrow{k_1} \mathrm{S}$$

MACROMODEL I

Typical values of SLn and SL for commercial nickel catalysts are 2-3 and 5-100, respectively (2,4).

Although Macromodel I is frequently used for the calculation of selectivities, it is understood that more realistic ones should be necessary to describe the hydrogenation network more accurately. One which incorporates every possible reaction step that may be observed in the liquid phase is given by the following lumped reaction network:



MACROMODEL II

With Macromodel II new selectivity ratios, *SLn* and *SL* are calculated with the ratios $(k_3 + k_5 + k_6)/(k_2 + k_4)$ and $(k_2 + k_4)/k_1$, respectively (5). In both cases, pseudo-monomolecular rate constants are used.

Given the complex nature of the reaction system, mass transport limitations may obscure the interpretation of intrinsic selectivities for catalytic processes. However, in a substantial part of the open literature related to liquid phase hydrogenation studies or modeling, mass transfer effects have not been considered (6).

Kinetic studies are simplified whenever diffusional effects are minimized or eliminated. Obtaining precise estimates for the various macrokinetic rate constants demands good reproducibility and the absence of the so-called induction times. Even in these cases, separate experiments using different reactant mixtures must be used to properly evaluate the relative reactivities of the oil constituents.

This rather tedious procedure has seldom been applied in vapor phase (7,8) or liquid phase (9) hydrogenations using fatty acid methyl esters as model compounds, but it enables us to distinguish between the methyl oleate (O) produced by the partial hydrogenation of methyl linoleate (L) and the one obtained from methyl linolenate (Ln); likewise, it grants a quantification of the methyl stearate (S) coming from the complete hydrogenation of each of the tri-, di- and mono-unsaturated species.

Recently, we have been able to estimate the complete set of global, pseudo first order rate constants (GPRC) of Macromodel II, relative to the methyl oleate hydrogenation rate, using a supported nickel catalyst and a mathematical treatment that naturally brings in every "shunt" reaction of the network (9). A broad range of experimental conditions was carefully chosen to guarantee the complete absence of extra or intra particle mass transfer limitations, as well as the total suppression of induction periods (10). Grau *et al.* (9) detailed the procedural aspects of the reaction modeling and/or data handling.

The model included not only the hydrogenation steps of unsaturated methyl esters but also the co-hydrogenation of Ln and the adsorption/desorption steps, which are not in chemical equilibrium under typical process conditions. Thus, the GPRC are parameters of a complex nature.

The corresponding values of the intrinsic selectivities and yields (i.e., those associated only with the adsorption/desorption and catalytic reaction steps) for each of the intermediate hydrogenation products of the network will be presented and analyzed in detail.

We wish to determine under which conditions (even under complete absence of mass transfer related artifacts) the research investigator or the plant operator can still obtain a set of parameters able to characterize the intrinsic selectivity of Ni catalysts through the processing of kinetic data with the conventional consecutive Macromodel I.

EXPERIMENTAL PROCEDURES

Materials. The fatty acid methyl ester mixtures required were obtained from linseed and sunflower seed oils, by means of urea concentration followed by fractional distillation at low pressure. A mixture of methyl linoleate and oleate (62.31 and 37.70 wt%, respectively) was used

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to study the hydrogenation of methyl linoleate, and another one with methyl linolenate, linoleate and oleate (85.88, 13.45 and 0.67 wt%, respectively) was used to analyze the hydrogenation of methyl linolenate. Hydrogen was Matheson U.H.P. grade. A commercial Ni/silica-alumina catalyst was employed [Girdler G-95 (United Catalyst Inc., Louisville, KY); 25 wNi/w cat.; $S_g = 185$ m^2/g, B.E.T., N2; mean particle diameter $= 2.5\ \mu m$, sedigraphy; mean pore diameter = 9 nm, N2 desorption].

Analytical methods. Samples were analyzed by GLC. Saturated and unsaturated methyl esters were separated with a 7 ft. × 1/8 in. stainless steel column packed with 15% DEGS-PS on 100/120 Gas Chrom Z (Applied Science Laboratories Inc., State College, PA). Methyl margarate was the internal standard. FID were employed and peak areas were automatically recorded and integrated.

Equipment and operating procedures. The reactants were hydrogenated in a 100 c.c., mechanically agitated, Parr mini-reactor (Parr Instrument Co., Moline, IL) furnished with a cup and cap (CAC) preactivation device. The CAC device becomes the hydrogenation reactor when the reaction begins (10). Temperature was measured with a Pt thermo-resistance. Cooling water flowing through an internal coil was combined with an electric oven driven by a PID control unit to keep the temperature within ± 0.5°C. Pressure was measured and controlled within ± 1 psig using a strain gage transducer.

The effect of temperature on selectivity was studied at 125, 140, 155 and 170°C for constant pressures of 40, 60 and 80 psig. The catalyst was preactivated with hydrogen for 2 hr under reaction conditions, using the CAC device, prior to each run. Aliquots of 40 c.c. of the reactant mixtures were hydrogenated with 0.02% wNi/w liquid, agitating at 1100 rpm to eliminate external mass transfer resistances. Two runs were made for each of the experimental conditions, and an excellent reproducibility was obtained.

Full details related to catalyst pretreatment, reproducibility of data and induction times suppression have been reported elsewhere (10).

Mass transfer effects. Under our experimental conditions, the external resistances for the hydrogen mass transfer were less than 0.01% of the measured overall resistance (10). The values of gas-liquid and liquid-solid resistances were less than 0.04 s and 0.02 s, respectively. This means that the hydrogen concentration at the external surface of the catalyst particles was less than a 0.4% of the solubility value, even for the maximum reaction rates measured.

The values of the liquid-solid mass transfer resistance for the methyl esters ranged from 0.25 to 0.48 s at 170 and 125°C, respectively. The methyl ester concentrations at the external surface were 0.2% of their value in the bulk solution. Consequently, external mass transfer effects were small enough to be neglected.

Internal mass transfer resistances were found negligible, too. The Weisz and Prater moduli, Φ, for the hydrogen and methyl esters were 0.019 and 0.017, respectively, at 80 psig and 170°C. Since $\Phi \ll 1$, according to the generalized Weisz and Prater criterion (11), there are no intraparticle mass transfer limitations.

A more detailed description related to the quantification of the mass transfer resistances in this system has been reported elsewhere (10).

Selectivities calculation from experimental data. Several methods based on consecutive reactions (Macromodel I) have been described (12-16). They allow the estimation of selectivities by means of simple correlations or plots which relate the selectivity parameters with the initial and final composition of the reaction mixture. More involved methods have also been reported (17,18); they use computer simulations of the reaction paths that are obtained by analyzing samples taken at various levels of the extent of reaction. Most frequently, the latter method merely tends to reproduce the observed behavior numerically, unless sophisticated algorithms are used because a simultaneous estimation of parameters is normally done (19).

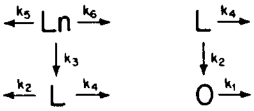
Instead, we have applied a methodology that complements experiences made with reactants of different (selected) compositions and a mathematical treatment which allows the uncoupling of the equations describing the reacting system; it also minimizes the correlation of errors of the estimated parameters and grants the elimination of self-contained information in the set of estimates.

It is well-known that a realistic description of the temporal distribution of reactants and products of the catalytic hydrogenation is attained with Langmuir-Hinshelwood type kinetic expressions (20,21). In this way, the reaction rates of the species in Macromodel II are given by:

$$\begin{aligned} r_{Ln} &= \phi\,\{(-k_3 - k_5 - k_6)\,C_{Ln}\} \\ r_L &= \phi\,\{k_3\,C_{Ln} - (k_2 + k_4)\,C_L\} \qquad [1] \\ r_O &= \phi\,\{k_3\,C_{Ln} + k_2\,C_L - k_1\,C_O\} \end{aligned}$$

where: $\phi^{-1} = 1 + K_{Ln}\,C_{Ln} + K_L\,C_L + K_O\,C_O$

The definition of a pseudo reaction time ($\tau = \phi\,t$) allows the analysis of the system as pseudo-monomolecular as well as its dissection into the following open subsystems (22):



SCHEME 1

Next, projection techniques and conventional linear algebra are used to manipulate rate data along straight reaction paths (9). Then, the full matrix of global pseudo first order rate constants (GPRC), relative to k_1, can be found:

$$K' = \begin{bmatrix} -(k'_3 + k'_5 + k'_6) & 0 & 0 \\ k'_3 & -(k'_2 + k'_4) & 0 \\ k'_5 & k'_2 & -1 \end{bmatrix} \qquad [2]$$

The sequential resolution of progressively more complex subsystems of Macromodel II (such as those depicted in Scheme 1) eliminates the simultaneous estimation of each of the macrokinetic parameters of the network.

TABLE 1

SLn Values for Hydrogenation of Methyl Linolenate[a]

Pressure (psig)	Temperature (°C)			
	125	140	155	170
40	6.66 ± 0.20	6.49 ± 0.11	6.34 ± 0.16	6.32 ± 0.30
60	6.72 ± 0.17	6.63 ± 0.17	6.48 ± 0.16	6.86 ± 0.06
80	6.71 ± 0.12	6.95 ± 0.17	7.01 ± 0.37	6.87 ± 0.16

[a]According to Macromodel II: $SLn = (k_3 + k_5 + k_6)/(k_2 + k_4)$.

TABLE 2

SL Values for Hydrogenation of Methyl Linoleate[a]

Pressure (psig)	Temperature (°C)			
	125	140	155	170
40	12.66 ± 0.17	14.70 ± 0.08	19.02 ± 0.27	25.76 ± 0.20
60	12.51 ± 0.14	14.45 ± 0.12	18.75 ± 0.14	25.22 ± 0.82
80	12.68 ± 0.13	14.17 ± 0.10	17.08 ± 0.35	22.79 ± 0.03

[a]According to Macromodel II: $SL = (k_2 + k_4)/k_1$.

The method yields the whole set of GPRCs in Eq. [2], and guarantees more reliable values for their estimates (9,22,23,24). Therefore, it is most suited for a selectivity analysis, as indicated below.

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the estimates of *SLn* and *SL* (for a 95% confidence interval) when Macromodel II is used to describe the reaction network.

SLn is not significantly modified by temperature changes, and mildly increases with higher hydrogen pressures. However, these values differ by more than 100% from those reported in previous works (3,4). Such a significative discrepancy is related to the use of a substantially different modeling of the hydrogenation reaction, since our model has a different level of apprehension of the phenomenon. We have included not only the hydrogenation steps of the Ln, L and O double bonds, but also the simultaneous co-hydrogenation of two double bonds of Ln, as well as adsorption/desorption steps which are not in chemical equilibrium under typical process conditions (9,22).

SL doubles when the reaction temperature is raised from 125 to 170°C; pressure increases slightly, attenuating this effect. Notice that *SL* is only slightly sensitive to pressure changes because it is composed of two additive terms, k_2/k_1 and k_4/k_1, with opposite pressure dependencies. The term k_2/k_1 diminishes, most noticeably at higher temperatures, at higher hydrogen pressures (9), which is in good agreement with mechanistic propositions (25). On the other hand, k_4/k_2 increases at higher pressures due to the enhancement of the shunt reaction L to S, which arises as a direct consequence of the relative increment of the hydrogenation rate of O respect its desorption rate (9). The values obtained are characteristic of nickel catalysts.

Figures 1 and 2 show that by using the calculated values of the GPRCs from Macromodel II, it is possible to fit compositional data for a full, wide range of conversions.

When the above mentioned mathematical methodology (9,23) was used employing Macromodel I (i.e., by imposing the restriction of "null shunts"), it was impossible to estimate a set of macrokinetic rate parameters able to describe the hydrogenation of both Ln-rich mixtures and L-rich ones. The consecutive reaction macromodel (Macromodel I) is unable to condense the information that is needed to correctly describe the evolution of concentrations in such a wide range of conversions. Its application may be successful for a limited range of these conversions. Even then the values of SLn and SL that it yields only approximate the true ones, *SLn* and *SL,* whenever the present tri-unsaturated fraction is below 10%, as analyzed in detail in Appendix A.

We have defined five selectivity parameters to quantify to which extent each of the species react towards lower levels of unsaturation while following the sequence of reactions indicated in Macromodel II, according to the concept:

$$S_{i\rightarrow j} = \frac{\text{reaction rate of species i to yield species j}}{\text{total reaction rate of species i}}$$

Then, for methyl linolenate (Ln), the following expressions were obtained:

$$\begin{aligned} S_{Ln\rightarrow L} &= k_3/(k_3 + k_5 + k_6) \\ S_{Ln\rightarrow O} &= k_5/(k_3 + k_5 + k_6) \qquad [3] \\ S_{Ln\rightarrow S} &= k_6/(k_3 + k_5 + k_6) \end{aligned}$$

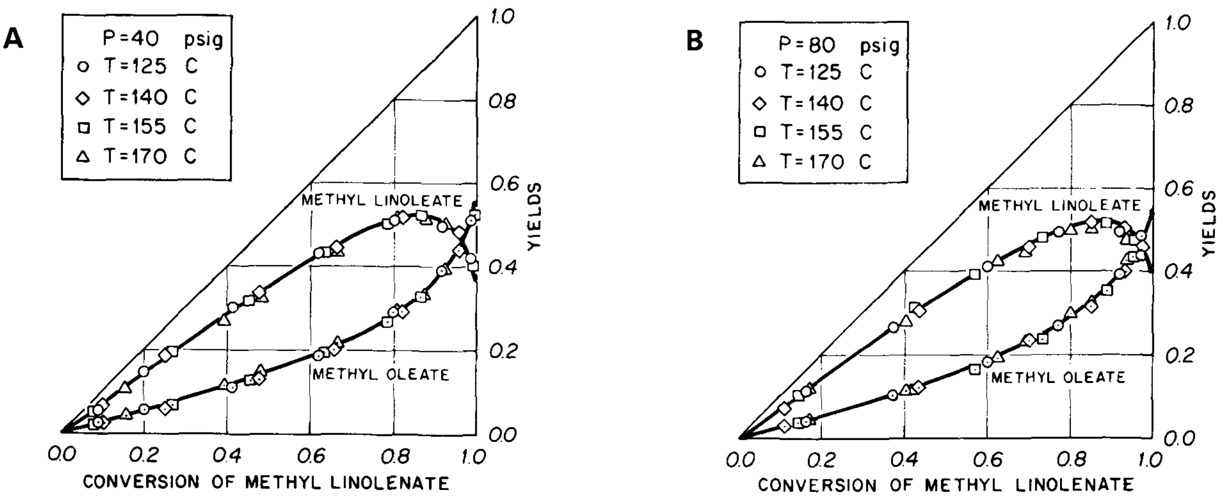


FIG. 1. Yields of methyl linoleate and methyl oleate during methyl linolenate hydrogenation at (A) 40 psig and (B) 80 psig. Full lines represent model predictions from Macromodel II.

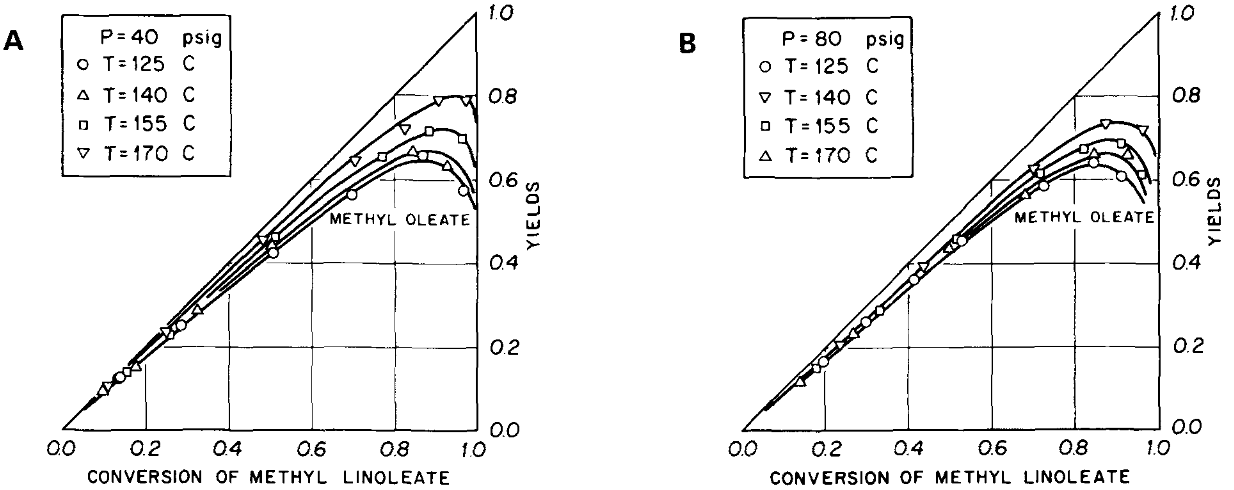


FIG. 2. Yield of methyl oleate during methyl linoleate hydrogenation at (A) 40 psig and (B) 80 psig. Full lines represent model predictions from Macromodel II.

Likewise, for methyl linoleate (L):

$$S_{L\rightarrow O} = k_2/(k_2 + k_4)$$
$$S_{L\rightarrow S} = k_4/(k_2 + k_4) \quad [4]$$

Tables 3 and 4 show the results obtained with Eqs. [3] and [4], for a 95% confidence interval. For example, it can be observed that for the explored reaction conditions, approximately 95% of L reacts to give O, whereas the remaining 5% shunts directly to produce S. These proportions suffer only minor changes with operating conditions: at 40 psig, temperature increases improve the L to O selectivity from 95% to 98%.

Both the magnitude of this selectivity and the above mentioned influence of the operating variables on it indicate that the direct conversion of L to S observed in the liquid phase arises merely as a consequence of a nonequilibrium chemisorption of the reactant, and is not a true co-hydrogenation on the catalyst surface. Our estimates of the corresponding apparent activation energies support this assertion (10).

Table 3 indicates that 79% of Ln reacts to yield L but also forms O directly (21% of the total disappearance of the reactant). These proportions do not change with either temperature or hydrogen pressure modifications. This high proportion of directly formed methyl oleate is a strong indication of a simultaneous co-hydrogenation of double bonds in Ln, which is also verified by looking at the apparent activation energy of the kinetic rate constant, k_5, representing the shunt. On the other hand, only at high temperatures and pressures is a similar direct hydrogenation of Ln to S is observed (a mere 1% of the Ln disappearance), again as a consequence of the nonequilibrium chemisorption of the triunsaturated species (10).

Figures 1 and 2 show the global effect of the reaction temperature and H_2 pressure on the production of

TABLE 3

Selectivity Values for Hydrogenation of Methyl Linolenate

Pressure (psig)	Temperature (°C) 125	140	155	170	
40	0.79 ± 0.03	0.80 ± 0.02	0.80 ± 0.02	0.79 ± 0.06	$S_{Ln \to L}$
60	0.77 ± 0.03	0.80 ± 0.03	0.79 ± 0.03	0.78 ± 0.04	
80	0.77 ± 0.01	0.77 ± 0.03	0.77 ± 0.01	0.77 ± 0.02	
40	0.21 ± 0.01	0.19 ± 0.01	0.20 ± 0.01	0.20 ± 0.01	$S_{Ln \to O}$
60	0.22 ± 0.01	0.20 ± 0.01	0.20 ± 0.01	0.21 ± 0.01	
80	0.22 ± 0.01	0.22 ± 0.01	0.21 ± 0.01	0.22 ± 0.01	
40	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	$S_{Ln \to S}$
60	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	
80	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	

TABLE 4

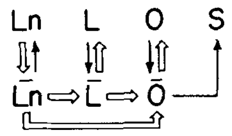
Selectivity Values for Hydrogenation of Methyl Linoleate

Pressure (psig)	Temperature (°C) 125	140	155	170	
40	0.95 ± 0.03	0.94 ± 0.01	0.95 ± 0.01	0.98 ± 0.02	$S_{L \to O}$
60	0.94 ± 0.02	0.93 ± 0.02	0.95 ± 0.01	0.96 ± 0.01	
80	0.95 ± 0.02	0.94 ± 0.01	0.94 ± 0.01	0.95 ± 0.01	
40	0.05 ± 0.03	0.06 ± 0.01	0.05 ± 0.01	0.02 ± 0.02	$S_{L \to S}$
60	0.06 ± 0.02	0.07 ± 0.02	0.05 ± 0.01	0.04 ± 0.01	
80	0.05 ± 0.02	0.06 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	

intermediates from methyl linolenate. Figure 1 clearly shows that these operation variables are unable to modify the relative amounts of L and O as long as Ln exists in appreciable amounts in the system. However, once Ln is depleted, Figure 2, the fraction of O produced from L, is sensitive to changes in the process variables, increasing at high temperatures and lower pressures.

This last observation, which is firmly established (2), is now quantified in this work under entirely reproducible conditions for reaction regimes controlled exclusively by the kinetic steps of the catalytic process. At 40 psig, the amount of methyl oleate produced in the reactor does not vary with temperature changes, while the triunsaturated reactant Ln exists in the liquid phase, but it can be 30% higher at 170°C than that produced at 120°C when the total content of Ln becomes negligible. Similarly, increases in the total pressure from 40–80 psig at 170°C, for instance, will cause either no changes or lesser amounts of methyl oleate to be formed (7.5%) according to whether or not Ln persists in the mixture.

From these experimental data, and bearing in mind that the rate of production of the different species in the system depends both upon the various hydrogenation rate constants and their relative concentrations on the catalytic surface, we can offer a sound quantitative confirmation of the usual hypothesis of the triunsaturated esters being much more adsorbed on the surface than their di- or monounsaturated counterparts. Thus, Ln preferentially covers the catalytic surface—even at low concentration in the liquid phase—and drives the hydrogenation process until it is almost completely consumed. Under these conditions the sequence of superficial reactions depicted in Scheme 2 prevails.



SCHEME 2

The apparent activation energies (relative to hydrogenation of O) of the macrokinetic steps representing hydrogenations in the complete macromodel (Macromodel II) are very similar: Ek_2 = 24.3 kJ/mole; Ek_3 = 21.3 kJ/mole and Ek_5 = 20.5 kJ/mole, at 40 psig (9). They readily account for the almost void effect of temperature on the relative distribution of unsaturates during the course of the reaction. Also, as long as the surface is kept covered with adsorbed Ln, this triunsaturated species attenuates any effects on the surface concentration of hydrogen that might be provoked by increases in the total pressure. Briefly, neither temperature nor pressure modifications are capable of altering the selectivities of the process as long as the methyl linolenate conversion is low.

At high Ln conversions, and naturally during the hydrogenation of methyl linoleate as the predominant feed of the mixture, the dominant macrokinetic steps are those characterized with k_1, k_2 and k_4 of Macromodel II, which indeed have different apparent activation energies: $Ek_2 = 24.3$ kJ/mole and $Ek_4 \cong 0$ kJmol, at 40 psig (22). Therefore, any temperature change is now able to modify the relative distribution of species, as described above. An alteration in hydrogen pressure will also modify the *SL* selectivity then, as explained by well-known mechanisms (25).

Thus, this work presents carefully controlled experimental data which were rigorously designed and processed. It confirms that the existence of a preferential adsorption of Ln and a significant co-hydrogenation of its double bonds characterize its hydrogenation on the catalyst surface, so that only structural changes of the latter (modifying the surface density of active catalytic sites) seems to be able to avoid the shunt reaction Ln to O. Moreover, this structural tailoring of the hydrogenation catalyst would not affect the *SL* selectivity, since the co-hydrogenation of L to Oseemingly observed in the liquid phase is only an artifact merely related to the nonequilibrium adsorption of the unsaturated species of the mixtures. Finally, it is shown that, for the evaluation of the true selectivity parameters of Ni catalysts using reaction data taken from the hydrogenation of Ln-rich mixtures (Ln > 10%), it is necessary to use a kinetic macromodel which, at the very least, has to include the co-hydrogenation of Ln to O. Nevertheless, the SLn and SL values that are customarily obtained with the classical consecutive reactions network can account for the intrinsic selectivity of the catalyst whenever the contents of Ln is lower (Ln < 10%). The successful application of a simplified macromodel (such as Macromodel I) to study selectivity in moderately unsaturated oils (e.g., soybean oils) is thus rationalized. On the same grounds, its application to the analysis of hydrogenation data from drying oils (e.g., linseed oil) is not advisable.

APPENDIX A

For the full range of experimental conditions used in this work, the average values of linolenate and linoleate selectivities are 3.24 ± 0.20 and 4.97 ± 0.91, respectively, when Macromodel I is used to fit the experimental data corresponding to the hydrogenation of the Ln-rich mixture (85.88 wt% Ln, 13.45 wt% L and 0.67 wt% O), as shown in Tables A.1 and A.2. With these macrokinetic parameters arising from Macromodel I, a fairly good fit of the distribution of species vs Ln conversion was obtained, as indicated in Table A.3.

However, despite this "fairly good fit," the SL values do not account for the well-known dependence of the linoleate selectivity with both temperature and hydrogen pressure. This strongly indicates that the macrokinetic parameters arising from Macromodel I are mere fitting parameters.

We have rigorously verified that when resorting to the simplified, consecutive Macromodel I, the values of SLn and SL it yields can be interpreted as macrokinetic parameters that depend mainly on the catalytic activity only when they are estimated from hydrogenation experiments using mixtures with a low content of Ln. This can be readily seen by comparing the predictions of the relative reaction rates that come from Macromodel I and Macromodel II, as follows:

From Macromodel I:

$$-\frac{dC_{Ln}}{dC_O} = SL\,\frac{SLn\,(C_{Ln}/C_L)}{SL - (C_O/C_L)} \qquad [A.1]$$

TABLE A.1

SLn Values for Hydrogenation of Methyl Linolenate[a]

Pressure (psig)	Temperature (°C) 125	140	155	170
40	3.38 ± 0.11	3.44 ± 0.17	3.03 ± 0.2	3.22 ± 0.07
60	3.23 ± 0.13	3.44 ± 0.17	3.33 ± 0.07	3.22 ± 0.09
80	3.22 ± 0.13	3.33 ± 0.09	3.03 ± 0.25	3.22 ± 0.07

[a] According to Macromodel I: $SLn = k_3/k_2$.

TABLE A.2

SL Values for Hydrogenation of Methyl Linoleate[a]

Pressure (psig)	Temperature (°C) 125	140	155	170
40	6.06 ± 0.09	5.88 ± 0.12	4.17 ± 0.37	5.92 ± 0.07
60	5.00 ± 0.25	4.54 ± 0.25	5.00 ± 0.22	6.25 ± 0.17
80	4.17 ± 0.37	4.17 ± 0.35	4.21 ± 0.31	4.32 ± 0.30

[a] According to Macromodel I: $SL = k_2/k_1$.

TABLE A.3

Distribution of Species vs Ln Conversion

Conversion of Ln	Mass fraction of methyl linolenate Exper.	Theor.	% Error	Mass fraction of methyl linoleate Exper.	Theor.	% Error
0.1029	0.770	0.771	0.13	0.234	0.223	4.70
0.2785	0.620	0.619	0.16	0.364	0.355	2.47
0.5480	0.388	0.388	0.00	0.488	0.521	6.76
0.7668	0.200	0.200	0.00	0.558	0.593	6.27
0.9123	0.075	0.075	0.00	0.566	0.544	3.89

Experimental conditions: Temperature, 125°C; pressure, 60 psig.

From Macromodel II:

$$-\frac{dC_{Ln}}{dC_O} = \frac{\mathit{SLn}\,(C_{Ln}/C_L)}{(\mathit{SL} - k_4/k_2) - (C_O/C_L) - k_5/k_1\,(C_{Ln}/C_L)} \qquad [A.2]$$

It is obvious that when $k_6 = k_5 = k_4 = 0$, $\mathrm{SLn} = \mathit{SLn}$ and $\mathrm{SL} = \mathit{SL}$.

Even in the case of negligible extra and intraparticle mass transfer resistances, i.e., in a regime controlled solely by catalytic reaction steps, we have shown that Ln shunts are significant (9). Therefore, Eq. [A.2] explains the difficulty in trying to describe the relative reactivity of the species with only two parameters (*SLn* and *SL*).

We are in a position to quantify these shortcomings of Macromodel I by means of the values of the GPRCs that we have obtained using Macromodel II (9):

$$0.02 < k_4/k_2 < 0.07 \qquad [A.3]$$

$$17.56 < k_5/k_1 < 37.96 \qquad [A.4]$$

From the *SL* values in Table 2 and the inequality [A.3], it follows that, although

$$\mathit{SL} - k_4/k_2 \cong \mathit{SL} \qquad [A.5]$$

[A.1] will only approximate [A.2] whenever the ratio CLn/CL is kept low.

Finally, from the *SL* values in Table 2 and the inequality [A.4], it is apparent that the denominators in [A.1] and [A.2] will differ by less than 10% only when

$$\alpha^\circ = C_{Ln}/C_L \times 100 < 7\% \qquad [A.6]$$

Thus, the values of *SLn* and *SL* can only be acceptably estimated from Macromodel I whenever the contents of Ln and L satisfy this condition [A.6]. This is why the simplified, consecutive network (Macromodel I) has been successfully applied when studying the selectivity in the hydrogenation of soybean oil ($\alpha^\circ \cong 9$–12%). It is also apparent why in this appendix the values in Tables A.1 and A.2 are mere fitting parameters ($\alpha^\circ \cong 733$), and why any study of selectivity in the hydrogenation of lineseed oil with Macromodel I ($\alpha^\circ \cong 200$–350), would be unadvisable.

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