LETTER TO THE EDITOR

Reply to Comments on A Second-Order Model for Catalytic-Transfer Hydrogenation Of Edible Oils

Sir:

We have addressed the following six comments made by Dr. Dijkstra: (i) concern regarding expressing concentration of P in terms of A; (ii) possible role of oleate shunt; (iii) the order of the hydrogen reaction, especially with respect to formate concentration; (iv) confusion regarding kinetic expressions when olive oil is used; (v) explanation about the data provided in Figure 5, and (vi) numerical values of the frequency factors and activation energies.

(i) The concentration of P in terms of A facilitates elimination of the time variable t, and thus the derivation of analytical expressions for concentrations of species B and C in terms of A becomes possible. This approach is adopted for mathematical convenience and does not violate any physical or chemical principles inherent in the model proposed. It is not true that this approach has been shown to be invalid (1) as Dr. Dijkstra alleges. Consider the following expressions as an illustration: if $A = 25t^2$ and $P = 5t$, then one can state $A = P^2$.

(ii) The mechanism for the oleate shunt that was reported by Heldal and Frankel (2) for the palladium-catalyzed hydrogenation of methyl linoleate has not yet been shown to be valid for the system under investigation. The data used in our paper involve formate ion-catalyzed hydrogenation of oil at much lower temperature (80°C) and pressure (l atm) conditions than those used for Heldal and Frankel (2). Therefore, we have no reason to believe that the specific mechanism used by them will also be valid for the data set used in our investigation. The relevant data in the paper by Heldal and Frankel (2) show that for linoleate reduction [Fig. 6, Heldal and Frankel (2)], the rate constant for its reaction *via* the series mechanism (i.e., linoleate → monoenes → stearate) is 1300% greater than the corresponding rate constant for its reaction by the oleate shunt. Thus, neglecting the oleate shunt in our analysis is also justified according to the mechanism proposed by Heldal and Frankel (2).

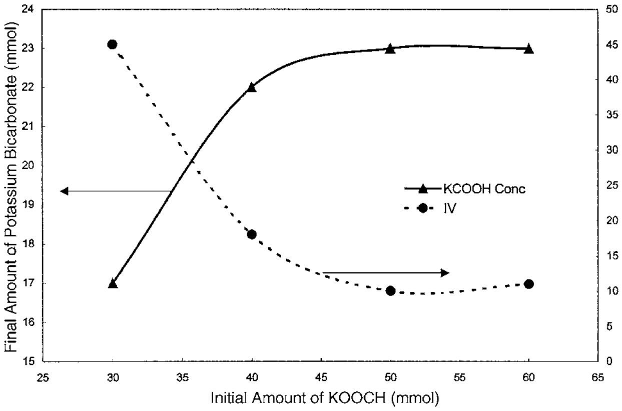

FIG. 1. Amount of formate consumed for hydrogenation and final iodine value (IV) vs. initial amount of formate. Initial IV = 133. Experimental data from Arkad *et al.* (3).

(iii) Figure 1 is a plot of potassium bicarbonate and iodine value vs. the initial amount of formic acid used based on the data from Arkad *et al.* (3). The data clearly show that the amount of the donor (i.e., formate) influences the extent of vegetable oil hydrogenation. It is seen that as the formate concentration is increased, the iodine value of the product (at the end of 16 h) decreases. The amount of formate consumed by reaction also increases with an increase in the formate concentration.

(iv) When olive oil is used, the rate of reduction is as follows:

$$\text{linoleic (A)} \xrightarrow{K_1} \text{oleic (B)} \xrightarrow{K_2} \text{stearic (C)} \qquad [1]$$

The above characterization of reduction pathway is consistent with our approach. There is no typing error involved as Dr. Dijkstra alleges.

(v) Figure 5 of our manuscript (4) was obtained by using Equation 18 and the experimental data provided in a paper by Naglič *et al.* (5). This figure shows that the rate of depletion of formate ion concentration by the hydrogenation of vegetable oil reaction can be used to evaluate the rate of hydrogenation. The oscillations in the data can be explained by some of the following considerations, which have found support in the published literature:

(a) formation of conjugate dienes [Naglič *et al.* (5) and Coenen (6)],

(b) the higher rate of double bond migration as compared to the rate of hydrogenation of dienes in the presence of conjugated dienes [Heldal and Frankel (2)],

(c) higher rates of hydrogenation of conjugated dienes as compared to the corresponding rates of hydrogenation to linoleic acid [Naglič *et al.* (5) and Heldal and Frankel (2)],

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TABLE 1
Constants for Hydrogenation Reaction Rates Second-Order Kinetics

	Activation energy (kJ/mol)		Frequency factor (mol%)$^{-1}$ (min)$^{-1}$	
	Leskovsek *et al.* (8)	Šmidnovik *et al.* (7)	Leskovsek *et al.* (8)	Šmidnovik *et al.* (7)
Linolenic acid	46.9	53.7	2109	1.53×10^5
Linoleic acid	56.0	60.6	6260	1.79×10^5
Oleic acid	58.1	14.9	696	1.54×10^{-2}

TABLE 2
Constants for Hydrogenation Reaction Rates First-Order Kinetics

	Activation energy (kJ/mol)		Frequency factor (min)$^{-1}$	
	Leskovsek *et al.* (8)	Šmidnovik *et al.* (7)	Leskovsek *et al.* (8)	Šmidnovik *et al.* (7)
Linolenic acid	47.9	56.2	3.1×10^5	2.9×10^6
Linoleic acid	40.6	48.8	5.7×10^3	5.4×10^4
Oleic acid	98.1	119.2	1.7×10^{11}	1.9×10^{14}

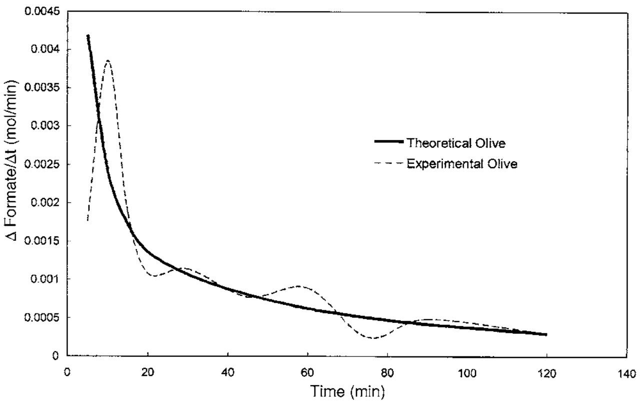

FIG. 2. Rate of change of formate ion concentration with time for olive oil hydrogenation. Comparison of theoretical and experimental values of fatty acid compositions.

(d) retardation of migration of double bonds in the presence of linolenic fatty acid [Naglič *et al.* (5)], and

(e) monopolization of catalyst active sites by higher-order unsaturated fatty acids [Coenen (6)].

However, based upon the constants obtained from fitting the model developed in our paper to the data by Naglič *et al.* (5), and using the theoretical expression developed in the paper (Eq. V of Table 1), a monotonically decreasing plot of the change in formate concentration vs. time is obtained (see Fig. 2). We do feel that the oscillating formate ion concentration vs. time plot (also presented in Fig. 2) is a more realistic representation because it is based upon the experimental data.

(vi) It is seen from the data provided in Figure 6 of our manuscript (4) that the r^2 value for the regression value of oleic acid hydrogenation rate constants is rather low. Therefore, it is indeed possible that the frequency factor and the activation energy values may contain a large degree of error. Table 1 presents the frequency factors and activation energies for linolenic, linoleic, and oleic acid that have been calculated using the second-order model. The experimental data used in the calculations were obtained from Šmidnovik *et al.* (7) and Leskovsek *et al.* (8). A large variation in the frequency factor as well as the activation energy is observed for the two sets of data in Table 1. The major reason for the variations in rate constants has to do with the fact that the reactions are heterogeneous and occur on the surface of the catalysts used, and therefore adsorption and mass transfer rates could play an important role in determining the overall rate of hydrogenation; however, the reactions are generally modeled using homogeneous reaction kinetics. The significant variations in the frequency factor and activation energy for the two sets of data are also observed when a first-order kinetic model is used as evidenced by the data presented in Table 2.

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