The influence of the isomerization reactions on the soybean oil hydrogenation process

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Abstract

Soybean oil has been partially hydrogenated in the presence of a synthesized nickel catalyst, in an industrial reactor, under the standard industrial working conditions. The GC measurements of fatty acids in the investigated oil and hydrogenated products have been performed. The total *trans* isomers content has been determined by the IR spectroscopy.

The model is established, which could be useful for the characterization of hydrogenation and isomerization reactions of poly-unsaturated acids. Iteration procedure, incorporating numerical simulation in each step is used to calculate rate constants of the proposed model from the comparison of the experimental and calculated kinetic runs. By the simultaneous treatment of the kinetic runs for the fatty acids composition and *trans*-isomer content, the 12 rate constants of individual hydrogenation and isomerization reaction steps are obtained. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Partial hydrogenation of the carbon-to-carbon double bonds in triglycerides, especially of vegetable oils, is a major industry in many parts of the world. Principal products, obtained by catalytic hydrogenation, include oleomargarines, shortening, soap stock and industrial greases and oils. Despite its importance, hydrogenation mechanism is not completely clarified, until now. The chemistry of triglycerides partial hydrogenation process is complicated. Both the mono- and poly-unsaturated acid groups in the oil hydrogenate at various rates, depending on the operating conditions. Furthermore, the geometrical and positional isomerization of the double bonds in mono- and poly-unsaturated acid groups occurs in significant numbers during the hydrogenation.

Attempts have been made in modeling of triacylglycerols hydrogenation process, with a reaction scheme allowing for hydrogenation and *cis–trans* isomerization [1]. The model used in this attempt was based on the reaction mechanism of mono-unsaturated acids. Therefore, it is not useful in the modeling of the consecutive hydrogenation steps, which lead to the hydro-

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genation of poly-unsaturated acids. A more adequate model is needed to describe the hydrogenation of the soybean oil.

The authors have already done some preliminary investigation of the soybean oil catalytic hydrogenation in the presence of a synthesized catalyst NICAT-2000 in an industrial reactor [2,3]. Concentrations of the fatty acids were being measured in the course of reaction time required for obtaining the commercially acceptable characteristics of a partially hydrogenated mass. The C_{18} fatty acids mass extent in the investigated oil and hydrogenated products have been performed by GC measurements [2]. The total *trans* isomers content during soybean oil hydrogenation has been determined through IR spectroscopy [3]. The hydrogenation and the isomerization rate constants have been estimated in separate steps, in a way, as those processes are independent of each other.

At first, only the hydrogenation rate constants were estimated in order to characterize the selectivity of the investigated catalyst. As it is a usual procedure in the characterization of the industrial process, the mechanism of the soybean oil catalytic hydrogenation reaction was, regarded as a series of consecutive stages:

$$C_{18:3} \xrightarrow{k_3} C_{18:2} \xrightarrow{k_2} C_{18:1} \xrightarrow{k_1} C_{18:0} \tag{1}$$
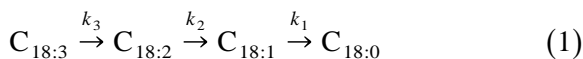
where $C_{18:3}$, $C_{18:2}$, $C_{18:1}$, and $C_{18:0}$ are linolenic, linoleic, oleic and stearic acids, respectively, and k_1, k_2, and k_3 are the corresponding rate constants. In order to apply a simple first approximation mathematical model, all the geometric and positional isomerization processes have been neglected. The rate constants k_3, k_2, and k_1 obtained from this model represent the cumulative rate constants of the process that incorporate a sum of all corresponding rates at which the particular geometric and positional isomers are being hydrogenated. Such cumulative rate constants for the unsaturated acids hydrogenation reactions have been determined and they are $k_3 = 2.88 \times 10^{-2}$ min^{-1}, $k_2 = 1.17 \times 10^{-2}$ min^{-1} and $k_1 = 1.98 \times 10^{-4}$

min^{-1}. According to these values, the used catalyst NICAT-2000 has demonstrated high activity and selectivity rates [2].

Further, the isomerization rate constant was evaluated. At the beginning of the hydrogenation process, almost all of the fatty acids are present in *cis* form. The *cis* isomer concentration logarithm exhibits a linear dependence on the reaction time. From its slope the cumulative rate constant of *cis* → *trans* transition is determined ($k^{ct} = 7.73 \times 10^{-3}$ min^{-1}). This cumulative rate constant incorporates a sum of all corresponding rate constants of the reactions at which particular fatty acids isomerize. Rate constant for only one direction of the isomerization process is obtained this way.

The aim of these further efforts was to obtain the best fitting values for the isomerization rate constant of *trans* → *cis* transition, k^{tc}. Since it has not been possible to measure the individual isomeric composition of each fatty acid, the following two assumptions have been accepted previously as the necessary approximation: (a) that the isomerization reaction for each of these fatty acids is going on at the same rate; and (b) that both the *cis* and *trans* isomers of any fatty acid participate in the hydrogenation process at equal rates. According to the accepted assumptions, the isomer form of molecules is not changed by the hydrogenation process and this is what additionally simplifies the model as related to a complex real system. For such a simplified model, a numeric simulation with the use of rate constants for a reversible isomerization reaction in a wide value interval (10^{-1} to 10^{-8} min^{-1}) has been chosen, using the cumulative hydrogenation constants. The results of the numeric simulation are compared with the experimental measurements of the total *trans* isomer content. Only the upper limit for k^{tc} was obtained, ($k^{tc} < 1.0 \times 10^{-3}$ min^{-1}). However, the obtained excellent agreement of the numeric results and the experiment is making it possible to use the obtained values for the characterization of the hydrogenation process selectivity in relation to a parallel isomerization [3].

Table 1
Starting values of the rate constants

i (min^{-1})	3	2	1
k_i^{ct}	7.73×10^{-3}	7.73×10^{-3}	7.73×10^{-3}
k_i^{tc}	1.00×10^{-3}	1.00×10^{-3}	1.00×10^{-3}
k_i^{c}	2.88×10^{-2}	1.17×10^{-2}	1.98×10^{-4}
k_i^{t}	2.88×10^{-2}	1.17×10^{-2}	1.98×10^{-4}

The obtained values for the isomerization rate constants represent some approximation. Further enhancements are possible through an improvement of the fitting process, which would open the possibility of using a more precise model with fewer approximations.

$$\begin{array}{c} C_{18:3}^{cis} \xrightarrow{k_3^c} C_{18:2}^{cis} \xrightarrow{k_2^c} C_{18:1}^{cis} \xrightarrow{k_1^c} \\ k_3^{ct} \Big\updownarrow k_3^{tc} \quad k_2^{ct} \Big\updownarrow k_2^{tc} \quad k_1^{ct} \Big\updownarrow k_1^{tc} \quad \mathbf{C}_{C18:0} \\ C_{18:3}^{trans} \xrightarrow{k_3^t} C_{18:2}^{trans} \xrightarrow{k_2^t} C_{18:1}^{trans} \xrightarrow{k_1^t} \end{array} \tag{2}$$

In this model, only one approximation is still preserved, which states that the hydrogenation reactions, by themselves, do not change the isomer composition. It seems that this last approximation does not leave any important constraints on the kinetic behavior, because the isomerization reactions with appropriate rate constant values could compensate for the effect of possible hydrogenation from *trans* to *cis* forms.

The present model involves 12 rate constants. To quantitatively analyze such a complex system and obtain reliable values of rate constants is an almost unsolvable task. However, the method used in Ref. [1] does not directly constrain the number of rate constants that could be evaluated. The object of this paper was to evaluate all 12 rate constants from the comparison of the experimental and calculated kinetic runs.

2. Experimental

Soybean oil (Yugoslav soy-bean variety), in the presence of a synthesized catalyst NICAT-2000 [2], has been partially hydrogenated in an industrial reactor (capacity: 5000 l) at the Factory of Edible Oils and Fats ''VITAL'' in Vrbas, under the standard industrial working conditions. The GC measurements of the fatty acids in the oil and hydrogenated products under study, have been performed on the model HP5890 series Plus. The total *trans* isomers content during the soybean oils hydrogenation (with NICAT-2000 catalyst) in an industrial reactor has been determined through IR spectroscopy (PE-983G).

The set of differential equations, corresponding to the investigated model, is solved numerically by the ODE45 algorithm. The rate constants are obtained from kinetic runs by minimizing the sums of squares of deviations between the calculated and experimental concentrations of fatty acids and *trans* isomers. The minimization is carried out by the simplex method. The minimization parameters are the values of the rate constants. It was necessary to approximately calculate the isomeric composition of the soybean oil, which corresponds to initial values for the numerical simulation. Therefore, the proportional distribution of the *trans* isomers between fatty acids of the raw soybean oil was assumed.

3. Results and discussion

The rate constants of all reactions involved in the complex hydrogenation process are optimized iteratively, to get the best fit of the experimental data with numerical simulation. The starting values of the rate constants were identical to published ones (Table 1).

Table 2
Isomerization rate constants, after the first iteration step

i (min^{-1})	3	2	1
k_i^{ct}	3.74×10^{-3}	8.32×10^{-4}	2.04×10^{-2}
k_i^{tc}	6.38×10^{-3}	2.70×10^{-4}	4.07×10^{-6}

Table 3
Hydrogenation rate constants, after the second iteration step

i (min^{-1})	3	2	1
k_i^{c}	4.83×10^{-2}	1.16×10^{-2}	1.47×10^{-4}
k_i^{t}	1.85×10^{-2}	2.30×10^{-2}	1.50×10^{-7}

In all tables, k_i^{ct} denotes the rate constant for $cis \rightarrow trans$ transition of the $C_{18:i}$ fatty acid, k_i^{tc} stands for $trans \rightarrow cis$ transition of the same acid, k_i^{c} and k_i^{t} are the hydrogenation rate constants of cis and $trans$ forms for the fatty acid with ''i'' double bonds.

Preliminary investigations implied that the efficiency of the iteration procedure is sensitive on the initial values of the rate constants. Large number of minimization parameters result in decreasing its efficiency. Therefore, rate constants are calculated in several steps. In the first step, only the isomerization constants have been determined approximately (Table 2).

In the next iteration step, the hydrogenation constants are refined (Table 3).

Finally, both the hydrogenation and isomerization rate constants are refined simultaneously to get the best fitting values.

The numerical simulation with this set of rate constants (Table 4) obviously gives better results for the total *trans* isomer content, than with initial ones, (Fig. 1a). At the same time, fatty acids composition is also well simulated (Fig. 1b).

The obtained isomeric distribution of the fatty acids (Fig. 2) is significantly different than the approximate calculation done previously [3]. This difference is a simple consequence of the fact that the present model allows the fact that
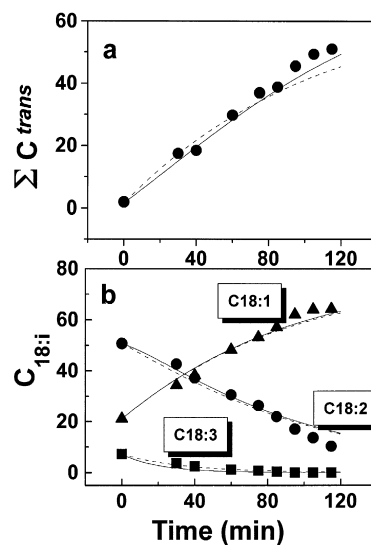

Fig. 1. Experimental results (symbols) and the numerical simulation with initial (dashed line) and final values of rate constants (solid line). (a) Total *trans* isomer content in % wt. (b) Fatty acids composition in % wt.

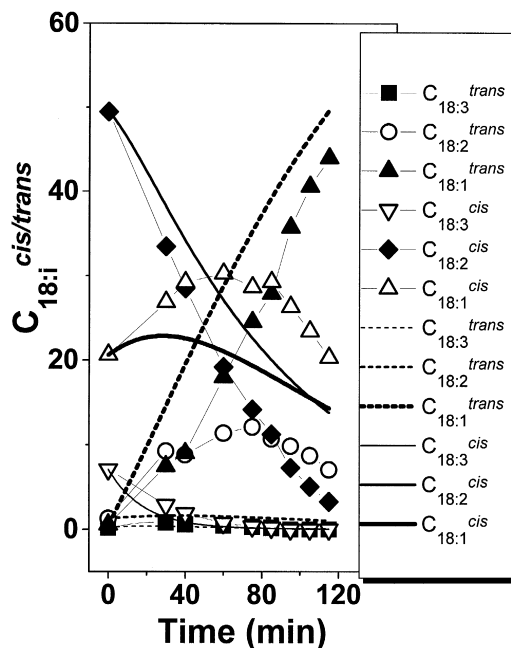different fatty acids could isomerize with different reaction rates.

Fig. 2. Calculated isomeric distribution based on the asumption of proportional distribution of *trans* isomers between the fatty acids (symbols connected with thin lines) and the numerical simulation with final values of rate constants for different fatty acids (lines without symbols).

Table 4
Rate constants, after the final iteration step

i (min^{-1})	3	2	1
k_i^{ct}	3.91×10^{-3}	8.06×10^{-4}	1.98×10^{-2}
k_i^{tc}	6.09×10^{-3}	2.82×10^{-4}	3.92×10^{-6}
k_i^{c}	5.00×10^{-2}	1.17×10^{-2}	9.74×10^{-5}
k_i^{t}	1.92×10^{-2}	2.10×10^{-2}	9.62×10^{-8}

For the isomerization rate constants, comparably small values are obtained in all cases except for rate constant k_1^{ct}. The small values obtained imply that isomerization is proceeding through the catalytic hydrogenation process and is dependent on the availability of active site. The strong influence of the isomerization reaction is obtained in the case of oleic acid, which is significantly transformed in *trans* isomer. This process improves the catalyst selectivity toward the oleic acid since the *trans* isomer of this acid seems to be less sensitive to further hydrogenation (Table 4). The isomerization rate constants obtained for linoleic acid indicate that this process is slow and directed toward the more reactive *trans* isomer. Therefore, the isomerization should have partially promotional effect on this step of the hydrogenation process.

4. Conclusion

The iteration procedure, which incorporates numerical simulation in each step, enables us to use a more realistic model. By the simultaneous treatment of the kinetic runs for the fatty acids composition and *trans*-isomer content, the rate constants of individual reaction steps are obtained.

The results gained in this procedure are very informative on the reaction pathways, which could possibly dominate in a complex mechanism. According to the values of the rate constants obtained, only oleic acid is subjected to intensive isomerization and linoleic acid has an especially slow isomerizing stage during hydrogenation in the investigated catalyst.

The influence of the catalyst and process parameters on hydrogenation and isomerization rates will be a subject for future work.

The new experiments are needed now to check for the detailed isomer distribution, which is predicted by the model. There is a leak in experimental and theoretical efforts in the field of the reactor dynamics, which could have strong influence on the reaction rates.

Acknowledgements

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