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## Hydrogenation of edible oils and fats

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RIJKSUNIVERSITEIT GRONINGEN

# **Hydrogenation of edible oils and fats**

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## Abstract

This thesis is a stepwise investigation of the hydrogenation of edible oils over silica-supported-nickel catalysts, starting from the hydrogenation and isomerization of a single double bond, whereafter reactions of double unsaturated bonds and the influence of intraparticle diffusion limitation is incorporated. Knowledge on these subparts of the hydrogenation process leads to a more selective hydrogenation of edible oils, thereby suppressing unwanted sideproducts.

The monounsaturated fatty acid methyl ester (FAME) was recognized as the basic reactant. First, by a wide range of experiments, the intrinsic surface reaction kinetics of the hydrogenation of the monounsaturated FAME were determined by a statistical evaluation of the most likely rate-determining reaction steps. Then, the reaction scheme was extended to double unsaturated FAME by addition of a single adsorption parameter only. This adsorption parameter was fitted from experimental data.

The selected intrinsic rate equations of monoenic FAME hydrogenation were also applied for obtaining intraparticle effective diffusion coefficients ( $D_e$ ) of triacylglycerides (TAG) and hydrogen from batch hydrogenations at elevated temperatures. Independent data on  $D_{e,TAG}$  was obtained from tracer pulse column experiments with the supported nickel. The latter experiments and separate batch adsorption experiments delivered information on the adsorption of mono- and double unsaturated FAME on the catalyst as well.

In conclusion, the silica-supported-nickel catalyst, applied for edible oil hydrogenation, was investigated with respect to the intrinsic **monoene** and **diene** FAME **kinetics**, **intraparticle diffusion** and **adsorption**, of which the results will be summarized below.

**Monoene kinetics.** The monoenic FAME hydrogenation and isomerization over a supported nickel catalyst (Pricat 9910, sample 1992, particle diameter,  $d_p = 8.4 \text{ }\mu\text{m}$ ) was studied at  $0.02 \leq P_{H_2} \leq 0.50 \text{ MPa}$  and  $333 \leq T \leq 443 \text{ K}$ . Batch hydrogenations at constant and variable hydrogen pressure were carried out to investigate the rate-determining steps.

On the basis of the well-known Horiuti–Polanyi mechanism, involving a half-hydrogenated surface intermediate, kinetic rate equations were systematically derived

in this thesis following the Langmuir–Hinshelwood–Hougen–Watson approach. Each set of rate equations was tested by means of a  $c^2$  method on its ability to describe the experimental curves simultaneously. The  $c^2$  was minimized by a stepwise optimization of model parameters. Furthermore, we used Bartlett’s test to reduce the set of most-likely rate expressions.

The statistically most significant model assumes the formation of the half-hydrogenated surface intermediate as the rate-determining step and an equilibrium associative hydrogen adsorption. The rate equations are:

$$R_O = m_c \frac{-(-k_{f,O}^{O,h} + K_{iso} \bar{k}^{iso})C_O + \bar{k}^{iso} C_E}{C_O + C_E + (K_S / K_M)C_S} K_H P_{H_2} \quad (1)$$

$$R_E = m_c \frac{-(k_{f,E}^{E,h} + \bar{k}^{iso})C_E + \bar{k}^{iso} K_{iso} C_O}{C_O + C_E + (K_S / K_M)C_S} K_H P_{H_2} \quad (2)$$

with  $k_{f,O}^{O,h}$ ,  $k_{f,E}^{E,h}$ , and  $\bar{k}^{iso}$  (units: [mol/kg<sub>Ni</sub> s]) the formation of constants of the half-hydrogenated intermediate in the hydrogenation of *cis*-monoene and *trans*-monoene and in the isomerization path, respectively.  $K_{iso}$  is the equilibrium constant for the isomerization,  $K_S/K_M$  is the ratio of adsorption constants of saturated and monoene components,  $m_c$  is the catalyst load [kg<sub>Ni</sub>/m<sub>l</sub><sup>3</sup>],  $C_O$ ,  $C_E$ , and  $C_S$  are the concentrations of methyl oleate (*cis*), methyl elaidate (*trans*), and methyl stearate, respectively [mol/m<sub>l</sub><sup>3</sup>],  $K_H$  is the adsorption constant of hydrogen [MPa<sup>-1</sup>], and  $P_{H_2}$  [MPa] is the hydrogen pressure. The activation energies of  $K_H k_{f,O}^{O,h}$ ,  $K_H k_{f,E}^{E,h}$ , and  $K_H \bar{k}^{iso}$  are 32.2, 28.1, and 47.2 kJ/mol, respectively.

**Diene kinetics.** The kinetics of the hydrogenation of double unsaturated FAME over a nickel catalyst were studied in a batch hydrogenation autoclave. Experiments with constant hydrogen pressure were performed at  $323 \leq T \leq 363$  K and  $0.3 \leq P_{H_2} \leq 3.5$  MPa with Pricat 9910. Similar to the monoene FAME experiments, composition versus time data were obtained from these experiments via gas chromatographic analysis of the liquid phase. Variable pressure hydrogenation experiments provided pressure drop versus time data, from which hydrogenation rates as a function of the hydrogen pressure were determined.

Rate equations for the hydrogenation of double unsaturated FAME based on an extension of eqs 1 and 2 proved to be applicable for describing the product distribution

as a function of time. Also, the hydrogenation and the *cis*–*trans* isomerization rate constants observed for monounsaturated esters appeared to be relevant to double unsaturated esters hydrogenation as well. The experimentally observed high selectivity  $S_I$ , defined as the ratio of the hydrogenation rates of double unsaturated FAME over monounsaturated FAME could be explained quantitatively from strong adsorption of double- relative to monounsaturated esters. Selectivities of  $3.1 \leq S_I \leq 5.2$  were found for  $323 \leq T \leq 363$  K. The model proposed also proved capable of describing literature data of others equally well.

**Intraparticle diffusion** limitation in the hydrogenation and isomerization of FAMES and TAGs in porous nickel catalyst was investigated both under reactive and under inert conditions.

Under reactive conditions, the intraparticle diffusion coefficients were determined from the best fits of the model simulations applying the intrinsic reacting kinetics of monounsaturated FAME hydrogenations (eqs 1 and 2) to experiments under diffusion limited conditions. For  $0.02 \leq P_{H_2} \leq 0.50$  MPa, an effective hydrogen diffusion coefficient of  $D_{e,H_2} = (1.6 \pm 0.7) \times 10^{-10}$  m<sup>2</sup>/s ( $T = 443$  K) was obtained in Pricat 9910 (sample 1992,  $d_p = 8.4$  mm).

TAG hydrogenations with Pricat 9910, at  $373 \leq T \leq 443$  K and  $0.30 \leq P_{H_2} \leq 0.50$  MPa, appear to be limited by diffusion limitation of TAG, yielding  $D_{e,TAG} = (4.5 \pm 2.2) \times 10^{-13}$  m<sup>2</sup>/s ( $T = 373$  K),  $(2.0 \pm 0.9) \times 10^{-12}$  ( $T = 403$  K), and  $D_{e,TAG} = (3.1 \pm 1.1) \times 10^{-12}$  m<sup>2</sup>/s ( $T = 443$  K). The temperature dependency of  $D_e$  follows the relation  $D_e h/T = 2 \times 10^{-7}$  (m<sup>2</sup> Pa)/K ( $h$  is the fluid viscosity, Pa s) for  $373 \leq T \leq 443$  K.

Independent determination of  $D_e$  in porous nickel catalyst (Pricat 9933, sample 1992: average particle diameter,  $d_p = 10$  mm) was performed with tracer pulse column experiments using the HPLC (high-performance liquid chromatography) technique, in the absence of reaction. The packed columns (length 0.05 and 0.10 m; diameter  $4.6 \times 10^{-3}$  m) were eluted with *n*-octane,  $3 \times 10^{-10} \leq \Phi_v \leq 80 \times 10^{-10}$  m<sup>3</sup>/s ( $h = 0.5$  mPa s), and MCT oil (medium C<sub>10</sub>–C<sub>12</sub> chain triglyceride,  $h = 17$  mPa s) in the temperature range  $313 \leq T \leq 353$  K. The response curves indicated a regular packing of the column. Intraparticle effective diffusivities were measured with more viscous MCT oil as an eluent:  $1.4 \times 10^{-11} \leq D_e \leq 2.7 \times 10^{-11}$  m<sup>2</sup>/s for methyl palmitate and  $4 \times 10^{-12} \leq D_e \leq 7 \times 10^{-12}$  m<sup>2</sup>/s for trioleate and soybean oil (95% confidence limit,  $T = 313$  K).

Due to the absence of reaction (hydrogenation of double bonds), the obtained  $D_e$  with the HPLC technique is volume averaged and thereby determined by the larger

intercrystalline pores (<30% of the total pore volume) only. Moreover,  $D_e$  measured under reaction conditions reflected the influence of the micropores, resulting in a 10-fold lower value.

**Adsorption** phenomena of mono- and double unsaturated FAME on supported-nickel (Pricat 9933) and pure (Raney-) nickel catalysts were investigated with respect to preferential adsorption and surface occupancy. For supported-nickel catalysts, the adsorption of the methyl ester group could be determined from the average residence time of tracer pulse experiments. With *n*-octane as an eluent, the adsorption enthalpy of methyl hexadecanoate ester, methyl palmitate, was measured as  $\Delta H = -42 \pm 5$  kJ/mol ( $313 \leq T \leq 353$  K).

The adsorption of double bonds of FAMEs under reaction conditions on activated pure (Raney-) nickel was studied in a special “shaken” (not stirred) reactor, developed to perfectly mix high catalyst loads in liquid up to 60 w/w%. In the time needed to get adsorption at equilibrium, also hydrogenation, isomerization and chain shortening (demethylation or hydrogenolysis) occurs. For a binary mixture, a calculation method was developed to distinguish between hydrogenation and adsorption effects.

For monoene mixtures, which can be defined as pseudo binary mixtures, the experimental data showed a selectivity factor of >100 of preferential adsorption of monoene, relative to saturated molecules. The occupancy of the surface was 2.2 nm<sup>2</sup> per monounsaturated molecule. The diene mixtures inevitably also contained monounsaturated as well as saturated molecules which introduced too many unknown parameters in the calculations. Therefore, a quantitative determination of the diene adsorption could not be achieved. However, from side-products, a preferential adsorption of dienes, relative to monoenes, could be detected, which is in line with the results of the diene hydrogenations.

The development of a reaction mechanism, starting from basic reaction steps for monoene and diene hydrogenation and isomerization, is a basis for the investigation of more complex reaction mechanisms of polyunsaturated edible oils and fats. Also, the presumed large influence of the intraparticle diffusion coefficient on the reaction selectivity is now quantitatively supported by a wide series of experiments, both under reaction and under inert conditions. These data enable a more selective hydrogenation of edible oils and fats by the optimisation of the process conditions and in the development of new catalysts.



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