

Article

Redundancy-Free Models for Mathematical Descriptions of Three-Phase Catalytic Hydrogenation of Cinnamaldehyde

Ekaterina Borovinskaya ^{1,2}¹ Technical University of Dresden, 01062 Dresden, Germany; ekaterina.borovinskaya@tu-dresden.de² Saint-Petersburg State Institute of Technology, Technical University, 190013 St. Petersburg, Russia

Abstract: A new approach on how to formulate redundancy-free models for mathematical descriptions of three-phase catalytic hydrogenation of cinnamaldehyde is presented. An automatically created redundant (generalized) model is formulated according to the complete reaction network. Models based on formal kinetics and kinetics concerning the Langmuir-Hinshelwood theory for three-phase catalytic hydrogenation of cinnamaldehyde were investigated. Redundancy-free models were obtained as a result of a step-by-step elimination of model parameters using sensitivity and interval analysis. Starting with 24 parameters in the redundant model, the redundancy-free model based on the Langmuir-Hinshelwood mechanism contains 6 parameters, while the model based on formal kinetics includes only 4 parameters. Due to less degrees of freedom of molecular rotation in the adsorbed state, the probability of a direct conversion of cinnamaldehyde to 3-phenylpropanol according to the redundancy-free model based on Langmuir-Hinshelwood approach is practically negligible compared to the model based on formal kinetics.

Keywords: hydrogenation of cinnamaldehyde; interval analysis; Langmuir-Hinshelwood mechanism; kinetic modeling; redundancy-free model; sensitivity analysis



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1. Introduction

The heterogeneously catalyzed selective hydrogenation of α,β -unsaturated aldehydes is an important reaction for industrial production of fine chemicals. This reaction is particularly common in the production of α,β -unsaturated alcohols, which are used in perfumery and pharmaceutical industries.

In 1934, Horiuti and Polanyi [1] proposed a multistage mechanism for the heterogeneously catalyzed alkenes hydrogenation on metallic catalysts, which is regarded as a classical approach for description of the selective hydrogenation of α,β -unsaturated aldehydes. According to this mechanism, it is postulated that the hydrogenation of unsaturated compounds proceeds via the intermediate formation of semi-hydrogenated intermediates. On this basis, Claus formulated a complex mechanism of metal-catalyzed hydrogenation of crotonaldehyde [2]. He discussed the concept of possible adsorption geometry of the reactant with the metallic surface and provided the formation of semi-hydrogenated intermediates, whereby side reactions were not taken into account.

Heterogeneously catalyzed hydrogenation of high-molecular α,β -unsaturated aldehydes is usually carried out as a three-phase reaction in a gaseous-liquid-solid system, which is conducted in a batch reactor. The reaction products remain in the reactor, increasing the probability of readsorption of the desired products and their further reaction.

In order to evaluate the catalyst performance for the hydrogenation reaction, knowledge about the microkinetics is necessary. For modelling of this reaction, the kinetic approach is often used, which takes into account the adsorption-desorption steps. Neri et al. formulated a kinetic model of liquid-phase hydrogenation of cinnamaldehyde over Ru/Al₂O₃ based on Langmuir–Hinshelwood type rate expressions [3]. Toebes et al. provided modelling of the hydrogenation of cinnamaldehyde over carbon nanofiber-supported

platinum catalysts based on the concentration–time experimental results. In agreement with the literature, Langmuir–Hinselwood–Hougen–Watson kinetics were chosen for the modelling [4]. Kinetic description of such reactions can be simplified by assuming that the surface reaction is the rate-determining step (Langmuir–Hinshelwood mechanism). However, if adsorption–desorption processes in the reaction system are very slow, the process limitation are to be described with a more complex model according to Hougen–Watson mechanism [5].

The reaction scheme proposed by Goupil et al. [6] can serve as a good basis for kinetic modelling of the hydrogenation of cinnamic aldehyde (Figure 1). Hydrogenation reaction of CAL to HCOL, COL, and HCAL involves five individual parallel and consecutive reaction steps. Hydrogenation of the C=O group of cinnamic aldehyde (CAL) causes building of cinnamyl alcohol (COL). The C=C group hydrogenation leads to formation of 3-phenylpropanal (HCAL). Further hydrogenation of either COL or HCAL provides formation of 3-phenylpropanol (HCOL) [7,8].

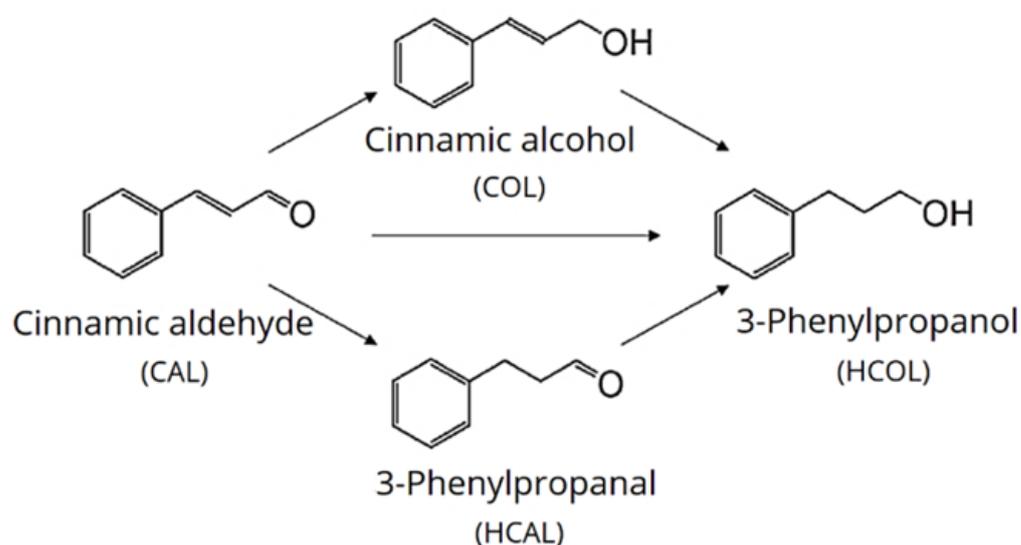


Figure 1. Simplified reaction scheme of the hydrogenation of cinnamic aldehyde according to Goupil [6].

The mechanism of the catalytic hydrogenation of cinnamic aldehyde is quite complex. Reaction rates can be usually determined based on theoretical conceptions about the mechanism of single reaction stages on the catalyst surface. It is extremely important to investigate scientifically based approaches for formulation of redundancy-free models of complex catalytic reactions in order to develop an efficient method of finding sufficient and reliable kinetic schemes. The idea of this paper is to provide a simplified reaction scheme of the three-phase catalytic hydrogenation of cinnamic aldehyde based on the generalized model description (GD), which was already demonstrated for the isomerization of n-decane [9].

2. Results and Discussion

The strategy for formulation of mathematical description of the three-phase catalytic hydrogenation of cinnamic aldehyde was used according to the procedure described in [10]. According to the principle “everyone with everyone”, an automatically created redundant GD was obtained (see Figure 2).

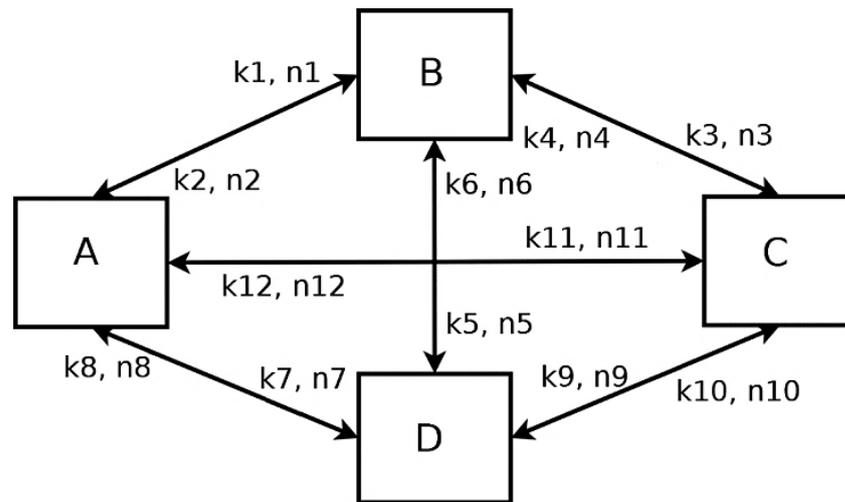


Figure 2. The redundant (generalized) model for the hydrogenation of cinnamaldehyde as a basis for the formulation of the redundancy-free model.

The model structure in Figure 2 can be described by the system of ordinary differential equations:

$$\begin{aligned}
 \frac{dC_A}{dt} &= -r_1 + r_2 - r_7 + r_8 - r_{11} + r_{12} \\
 \frac{dC_B}{dt} &= r_1 - r_2 - r_3 + r_4 - r_5 + r_6 \\
 \frac{dC_C}{dt} &= r_3 - r_4 + r_{11} - r_{12} - r_9 + r_{10} \\
 \frac{dC_D}{dt} &= r_5 - r_6 + r_9 - r_{10} + r_7 - r_8 \\
 C_A|_{t=0} &= C_{A,0} = 47.9 \text{ mol/L}, \\
 C_B|_{t=0} &= C_{B,0} = 0, \\
 C_C|_{t=0} &= C_{C,0} = 0.326 \text{ mol/L} \\
 C_D|_{t=0} &= C_{D,0} = 1.69 \text{ mol/L}
 \end{aligned} \tag{1}$$

where: C_i —the concentration of the i -th component in mol/L; r_j —the rate of the j -th reaction mol/s, defined as $r_j = k_j C_i^{n_i}$ with k_j —reaction rate constant and n_i —reaction order.

The component A represents CAL, B —COL, C —HCOL, and D —HCAL in Figure 1. Experimental kinetic data for the hydrogenation of cinnamic aldehyde on the catalyst Pt₇₀-Fe₃₀/SiO₂ at $T = 350$ °C are shown in Figure 3 [5].

2.1. Formal Kinetic Approach

In the first step, the ranges of the model parameter values were determined. For this purpose, the GD model calculation at different model parameter intervals was provided. The obtained value of the RSS at $k_i \in [0, 1]$, $n_i \in [0.55, 3]$ indicated that the reaction is inaccurately described by the model under the chosen conditions ($RSS = 1.0924$). On the other hand, the parameter values for $k_1, k_3, k_6, k_7, k_8, k_{11}, k_{12}$ are already at the interval limit. Some values for the determined reaction orders are also at the limit of the selected interval, but its further extension seems unfavorable from a physical-chemical point of view. Therefore, calculation experiments with extended interval limits for k_i were carried out (Table 1, 2nd test run). Many model parameters were still at interval limits, although the value of the RSS was significantly reduced.

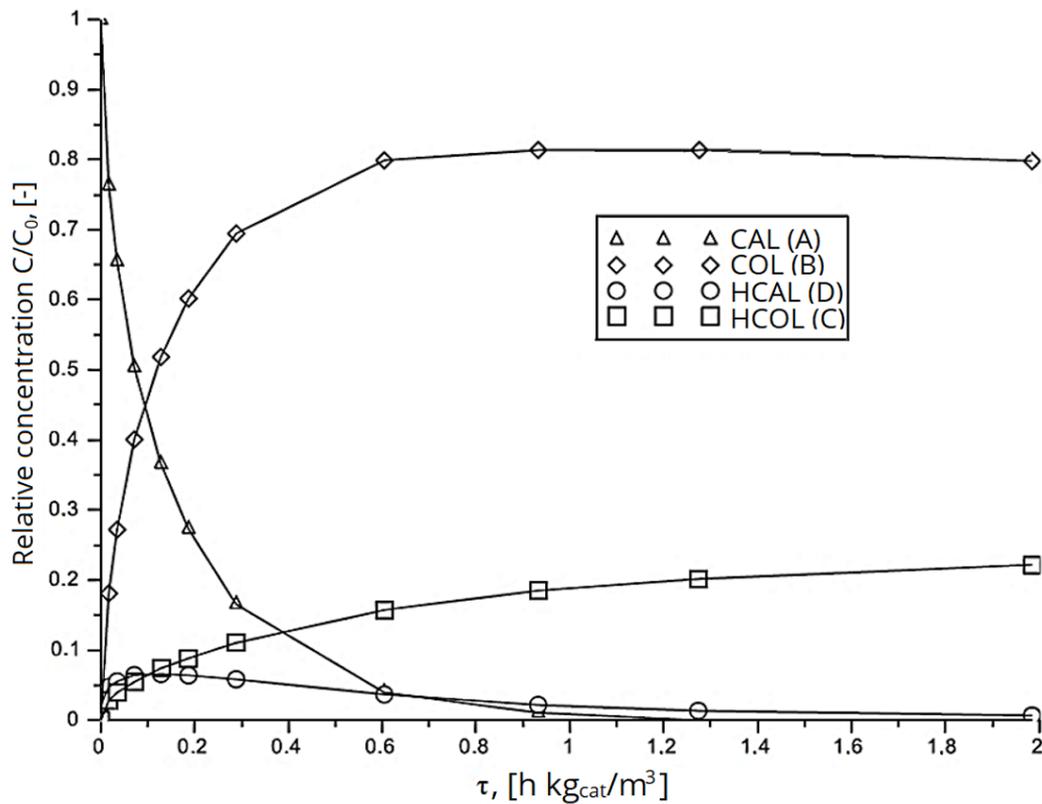


Figure 3. Experimental data of the hydrogenation of cinnamic aldehyde (Catalyst Pt₇₀-Fe₃₀/SiO₂, T = 350 °C) [5].

Table 1. Solution results of the kinetic inverse problem for the hydrogenation of cinnamic aldehyde based on formal kinetic approach.

Solution Interval	Determined Numerical Values for the Kinetic Constants k and Reaction Orders n	Equation Nr.	RSS
Test run 1			
$k_i \in [0,5]$, $n_i \in [0.55,3]$	$k_1 = 4.999$ $k_2 = 0.00169$ $k_3 = 0.0289$ $k_4 = 4.299$ $k_5 = 0.798$ $k_6 = 4.999$ $k_7 = 4.999$ $k_8 = 4.834$ $k_9 = 4.496$ $k_{10} = 0.913$ $k_{11} = 1.997$ $k_{12} = 0.885$ $n_1 = 1.008$ $n_2 = 2.672$ $n_3 = 0.769$ $n_4 = 2.815$ $n_5 = 0.550$ $n_6 = 0.550$ $n_7 = 2.508$ $n_8 = 1.471$ $n_9 = 2.995$ $n_{10} = 0.596$ $n_{11} = 2.999$ $n_{12} = 2.650$	(1)	0.0375
Test run 1a			
$k_i \in [0,5]$, $n_i \in [0.55,3]$	$k_1 = 4.999$ $k_2 = 0.00003$ $k_3 = 0.274$ $k_4 = 0.370$ $k_5 = 0.886$ $k_6 = 4.999$ $k_7 = 4.999$ $k_8 = 2.000$ $k_{11} = 2.472$ $k_{12} = 3.626$ $n_1 = 1.019$ $n_2 = 2.967$ $n_3 = 0.772$ $n_4 = 0.581$ $n_5 = 0.500$ $n_6 = 0.502$ $n_7 = 2.935$ $n_8 = 1.958$ $n_{11} = 2.983$ $n_{12} = 2.529$	(2)	0.0375
Test run 1b			
$k_i \in [0,5]$, $n_i \in [0.55,3]$	$k_1 = 4.999$ $k_5 = 0.8526$ $k_6 = 4.999$ $k_7 = 4.999$ $k_8 = 4.960$ $k_{11} = 0.996$ $k_{12} = 0.00009$ $n_1 = 1.1064$ $n_5 = 0.5038$ $n_6 = 0.5000$ $n_7 = 2.3408$ $n_8 = 1.1094$ $n_{11} = 0.828$ $n_{12} = 2.994$	-	0.0402
Test run 1c			
$k_i \in [0,5]$, $n_i \in [0.55,3]$	$k_1 = 4.999$ $k_5 = 9.638 \cdot 10^{-9}$ $k_7 = 0.804$ $k_{11} = 3.30473$ $k_{12} = 3.969 \cdot 10^{-5}$ $n_1 = 0.722$ $n_5 = 2.844$ $n_7 = 2.999$ $n_{11} = 2.695$ $n_{12} = 2.219$	(3)	0.1001

Table 1. Cont.

Solution Interval	Determined Numerical Values for the Kinetic Constants k and Reaction Orders n	Equation Nr.	RSS
Test run 1d			
$k_i \in [0,5]$, $n_i \in [0.55,3]$	$k_1 = 4.999$ $k_5 = 6.160 \times 10^{-9}$ $k_7 = 0.211$ $k_{11} = 1.349$ $k_{12} = 9.394 \cdot 10^{-8}$ $n_1 = 0.751$ $n_5 = 1$ $n_7 = 2.913$ $n_{11} = 1$ $n_{12} = 1$	(3)	0.1103
Test run 1e			
$k_i \in [0,5]$, $n_i \in [0.55,3]$	$k_1 = 5$ $k_5 = 1.907 \cdot 10^{-12}$ $k_7 = 0.143$ $k_{11} = 1.133$ $n_1 = 1$ $n_5 = 1$ $n_7 = 1$ $n_{11} = 1$	(3)	0.1270
Test run 2			
$k_i \in [0,100]$, $n_i \in [0.55,3]$	$k_1 = 6.771$ $k_5 = 3.675 \times 10^{-12}$ $k_7 = 0.199$ $k_{11} = 1.429$ $n_1 = 1$ $n_5 = 1$ $n_7 = 1$ $n_{11} = 1$ (the reaction orders n_1, n_5, n_7, n_{11} were not determined, but assumed to be 1)	(4)	0.0648

For more detailed analysis, Figure 4 provides a comparison of the model parameter values obtained in test runs (Table 1), which were normalized to the upper interval limit. Figure 5 compares the sizes of the corresponding parameter intervals. In the next step, based on the DoE, the following parameters of the optimization method were determined: the number of generated start points ($P_1 = 220$); the number of target function calculations ($P_2 = 500$); the number of times the found values are taken as start points to continue the search ($P_3 = 5$).

Figure 4 clearly shows that the parameter values for k_1, k_6, k_7, k_8 are at the upper limit of the interval in test runs 1 and 2. This means that neither in the parameter range $k_i \in [0, 1]$ nor in the interval range $k_i \in [0, 5]$ could characteristic parameter values be found. The reaction rate constant k_2 is close to zero in both cases, which means that it can be neglected. The constants k_5, k_9, k_{10} and the reaction orders n_5 and n_6 could also be excluded. In order to make a conclusion in this context, the extended parameter intervals were also analysed (Figure 5). The maximum intervals have parameters $k_4, k_8, k_9, k_{10}, k_{12}$, and $n_2, n_3, n_4, n_8, n_9, n_{10}, n_{12}$, so that they can be assumed to be negligible. The constants k_9 and k_{10} also take very small values (Figure 4). This means that, in conjunction with the associated reaction orders n_9 and n_{10} , they can also be ignored in the mathematical description of the hydrogenation reaction. Accordingly, the differential equation system (1) can be simplified as follows:

$$\begin{aligned}
 \frac{dC_A}{dt} &= -r_1 + r_2 - r_7 + r_8 - r_{11} + r_{12} \\
 \frac{dC_B}{dt} &= r_1 - r_2 - r_3 + r_4 - r_5 + r_6 \\
 \frac{dC_C}{dt} &= r_3 - r_4 + r_{11} - r_{12} \\
 \frac{dC_D}{dt} &= r_5 - r_6 + r_7 - r_8 \\
 C_A|_{t=0} &= C_{A,0} = 47.9 \text{ mol/L}, \\
 C_B|_{t=0} &= C_{B,0} = 0, \\
 C_C|_{t=0} &= C_{C,0} = 0.326 \text{ mol/L} \\
 C_D|_{t=0} &= C_{D,0} = 1.69 \text{ mol/L}
 \end{aligned} \tag{2}$$

The parameter values calculated using the simplified model (2) and the corresponding parameter value ranges are summarized in Table 1. Figures 4 and 5 show normalized values of the model parameters and their intervals for the model with 20 parameters (test run 1a).

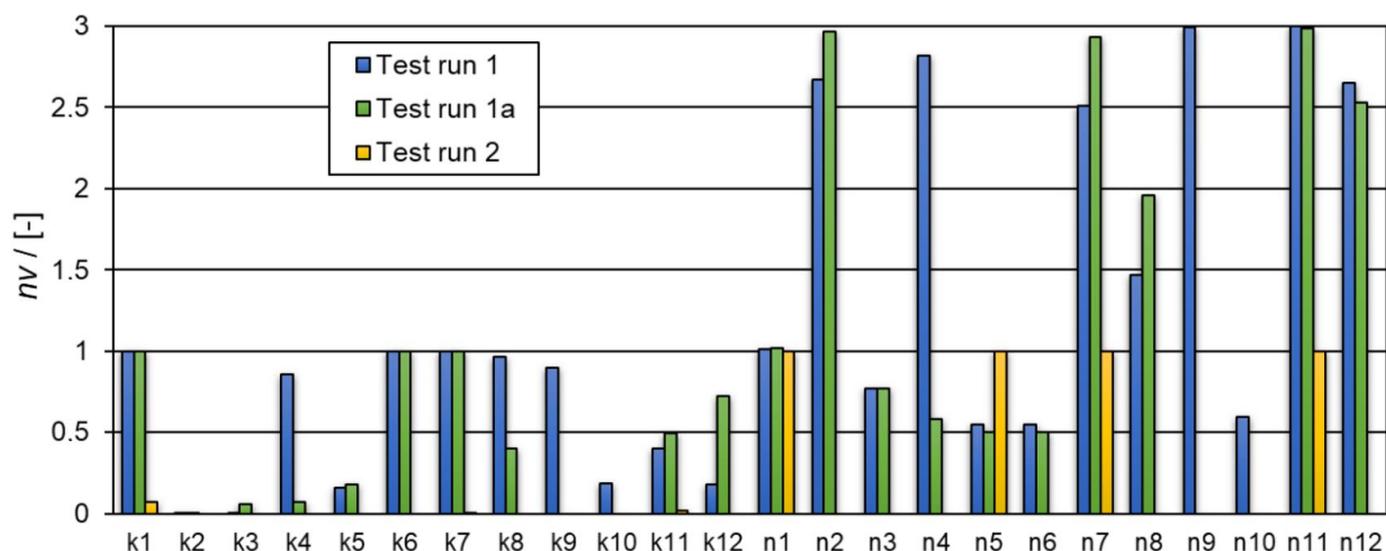


Figure 4. Parameter values for the models describing the cinnamic aldehyde hydrogenation in test runs 1, 1a and 2 for different solution conditions.

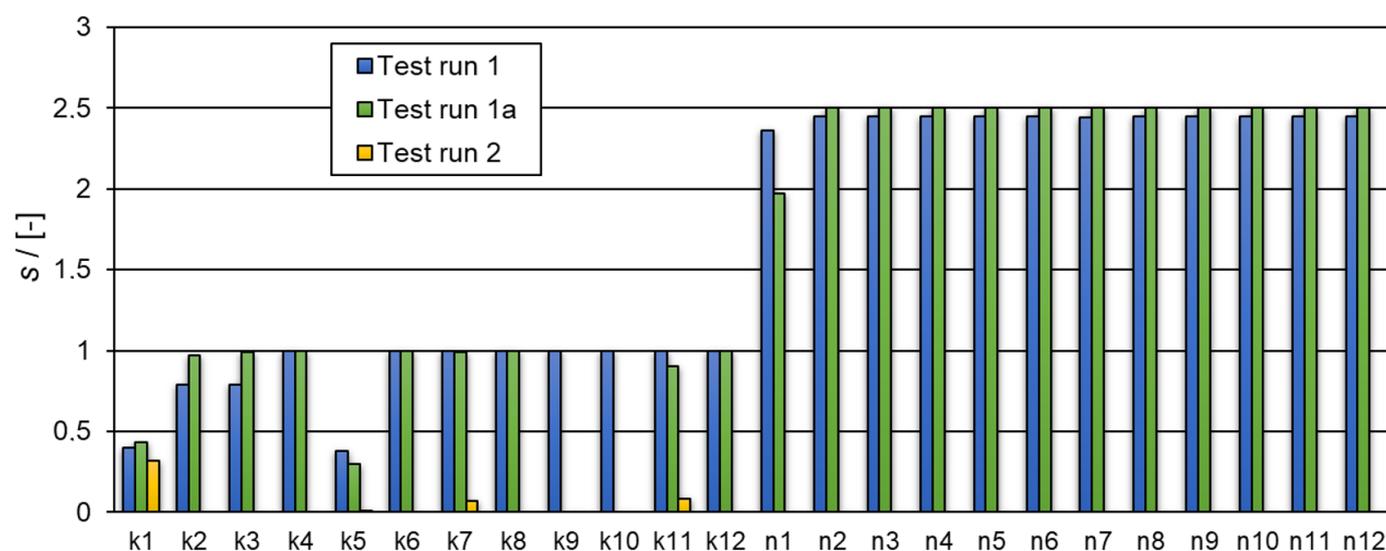


Figure 5. Parameter intervals calculated in test runs 1, 1a, and 2.

As a result of test run 1a, the minimum parameter value for the constant k_2 was found. At the same time, the constants k_2 – k_4 have the maximum size of the parameter intervals. Therefore, these parameters were excluded in the next model (test run 1b). In the test run 1b (Table 1), the parameter intervals for k_6 , k_8 and n_5 – n_{12} reached their maximum value. This shows that these parameters have little effect on the model output. The exclusion of the rate constants k_6 , k_8 , and the corresponding reaction orders n_6 , n_8 was realized in the model with 10 parameters:

$$\begin{aligned}
\frac{dC_A}{d\tau} &= -r_1 + r_2 - r_7 - r_{11} + r_{12} \\
\frac{dC_B}{d\tau} &= r_1 - r_2 - r_3 + r_4 - r_5 \\
\frac{dC_C}{d\tau} &= r_3 - r_4 + r_{11} - r_{12} \\
\frac{dC_D}{d\tau} &= r_5 + r_7 \\
C_A|_{t=0} &= C_{A,0} = 47.9 \text{ mol/L}, \\
C_B|_{t=0} &= C_{B,0} = 0, \\
C_C|_{t=0} &= C_{C,0} = 0.326 \text{ mol/L} \\
C_D|_{t=0} &= C_{D,0} = 1.69 \text{ mol/L}
\end{aligned} \tag{3}$$

As expected, the elimination of the model parameters k_6 , k_8 , n_6 , and n_8 leads to a certain decrease of the model accuracy; the *RSS* increases from 0.0375 to 0.0402.

In the following simplification step of model (3), the test runs 1c, 1d and 1e were performed (Table 1). The simplified, redundancy-free model structures are shown in Figure 6. The numerical values of the reaction orders determined in test runs 1c and 1d were set to 1 in test run 1e as a first approximation. Finally, test run 1e leads to the final version of a redundancy-free model based on the following differential equation system:

$$\begin{aligned}
\frac{dC_A}{dt} &= -r_1 + r_7 - r_{11} \\
\frac{dC_B}{dt} &= r_1 - r_5 \\
\frac{dC_C}{dt} &= r_{11} \\
\frac{dC_D}{dt} &= r_5 + r_7 \\
C_A|_{t=0} &= C_{A,0} = 47.9 \text{ mol/L}, \\
C_B|_{t=0} &= C_{B,0} = 0, \\
C_C|_{t=0} &= C_{C,0} = 0.326 \text{ mol/L} \\
C_D|_{t=0} &= C_{D,0} = 1.69 \text{ mol/L}
\end{aligned} \tag{4}$$

To check the performance of the resulting redundancy-free model, the ranges of the parameter values were extended: $k_i \in [0; 100]$ and $n_i \in [0.55, 3]$. The inverse kinetic task was solved in the test run 2 (Table 1). The obtained parameter values and their intervals are shown in Figures 3 and 4. Despite an extension of the parameter range, the values remained within the previously determined limits (see Table 1). Since the obtained sizes of the intervals are relatively small, it can be assumed that the remaining parameters are significant.

The quality of obtained models can be verified by information criteria. In Table 2, the characteristic criteria for all model approaches with the respective *RSS* are compared. Models 6 and 7 with the lowest number of parameters are among the best of the analyzed models (Table 2). They have the best values of the evaluation criteria: $AIC = \min$, $AIC_c = \min$, $\Delta_i = \Delta_{\min} \rightarrow 0$. Models 1 to 5, with $\Delta_i > 10$, are physico-chemically not very useful and do not represent experimentally observed dependencies adequately. The difference between models 6 and 7 is not the number of parameters or model structures, but rather the *RSS*, which is smaller for model 7 than for model 6 due to the widening of the model parameters range. The weights of the two models, calculated according to (17), are: $\omega_6 = 0.4247$, $\omega_7 = 0.5689$. Model 5 with $\omega_5 = 0.0063$ is not significant. The weights of models 1–4 cannot be taken into account, since $\omega_1 = \omega_2 = \omega_3 = \omega_4 = 0$.

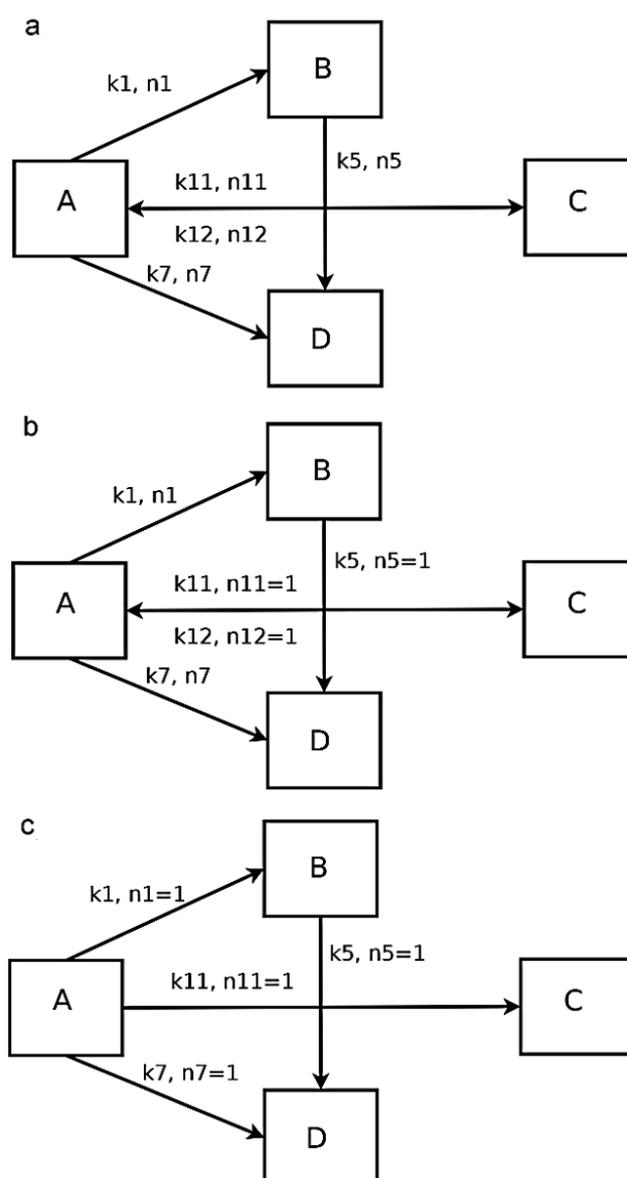


Figure 6. Simplified, redundancy-free models for the hydrogenation of cinnamic aldehyde formulated from a redundant model for the mathematical description of the reaction kinetics: (a) Test run 1(c), (b) Test run 1(d), (c) Test run 1(e).

Table 2. Evaluation of the model quality for mathematical description of the hydrogenation of cinnamic aldehyde according to the formal kinetic approach using information criteria.

Model-No.	Test Run	RSS	$\log(L(\hat{k}, \hat{\sigma}^2 \text{Daten}))$	N	AIC	AIC_c	$\Delta_i AIC_c$	ω_i
1	1	0.0375	67.53	25	43.86	116.08	110.17	0.0000
2	1a	0.0375	67.53	21	35.86	77.86	71.95	0.0000
3	1b	0.0402	66.86	15	23.92	41.06	35.15	0.0000
4	1c	0.1000	58.16	11	16.71	24.96	19.05	0.0000
5	1d	0.1103	57.22	8	10.80	14.91	9.00	0.0063
6	1e	0.1270	55.87	5	4.92	6.50	0.58	0.4247
7	2	0.0648	62.30	5	4.34	5.92	0.00	0.5689

Based on analysis of weight ratios between the models ω_7/ω_j : $\omega_7/\omega_6 = 1.34$, $\omega_7/\omega_5 = 89.89$, model 7 can be identified as the best model. The slight advantage of model 7 over model 6 is achieved, as already explained, by extending the range of parameter values, since the number of model parameters is not different for both models. Due to a small number of model parameters in both models, they are characterized by a high degree of clarity and, can optimally describe the kinetics of the hydrogenation in agreement with the formal-kinetic model according to (4).

2.2. Kinetic Approach according to Langmuir-Hinshelwood Mechanism

The redundant model (1) of the cinnamic aldehyde hydrogenation was provided according to the Langmuir-Hinshelwood mechanism. The rate of the individual reaction stages was defined by Equation (11). The test runs according to Langmuir-Hinshelwood mechanism are summarized in Table 3.

The first test run provides values for nine model parameters, which are located at the upper range and thus the range is to be extended. After the second test run, five parameters still reach the upper range. For this reason, the parameter range was extended by a further number of times as follows: $k'_i \in [0; 100]$ and $K_j \in [0; 100]$. As expected, with the extension of the range of the model parameters the value of the objective function RSS significantly decreases (Table 3, Figure 7).

According to the analysis of parameter values and parameter intervals determined in the 4th test run (Figures 7 and 8), the model parameters k_6 , k_9 , k_{12} , K_2 and K_3 can be excluded from further consideration. Thus, the differential equation system (1) can be simplified:

$$\begin{aligned}
 \frac{dC_A}{dt} &= -r_1 + r_2 - r_7 + r_8 - r_{11} \\
 \frac{dC_B}{dt} &= r_1 - r_2 - r_3 + r_4 - r_5 \\
 \frac{dC_C}{dt} &= r_3 - r_4 + r_{11} - r_{12} + r_{10} \\
 \frac{dC_D}{dt} &= r_5 - r_{10} + r_7 - r_8 \\
 C_A|_{t=0} &= C_{A0} = 47.9 \text{ mol/L}, \\
 C_B|_{t=0} &= C_{B0} = 0, \\
 C_C|_{t=0} &= C_{C0} = 0.326 \text{ mol/L} \\
 C_D|_{t=0} &= C_{D0} = 1.69 \text{ mol/L}
 \end{aligned} \tag{5}$$

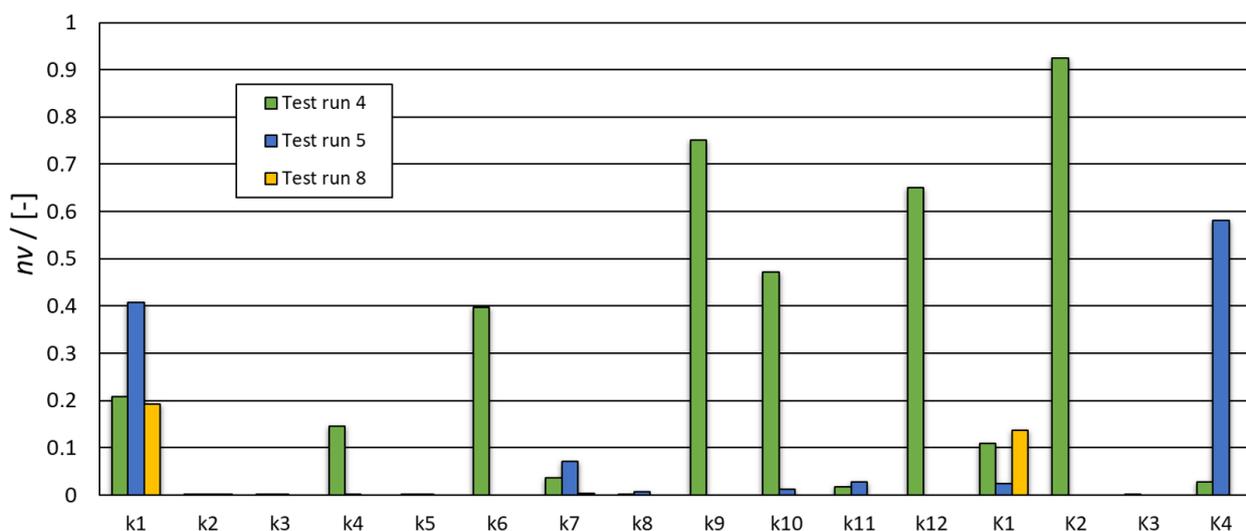


Figure 7. Parameter values determined according to (1) and (5).

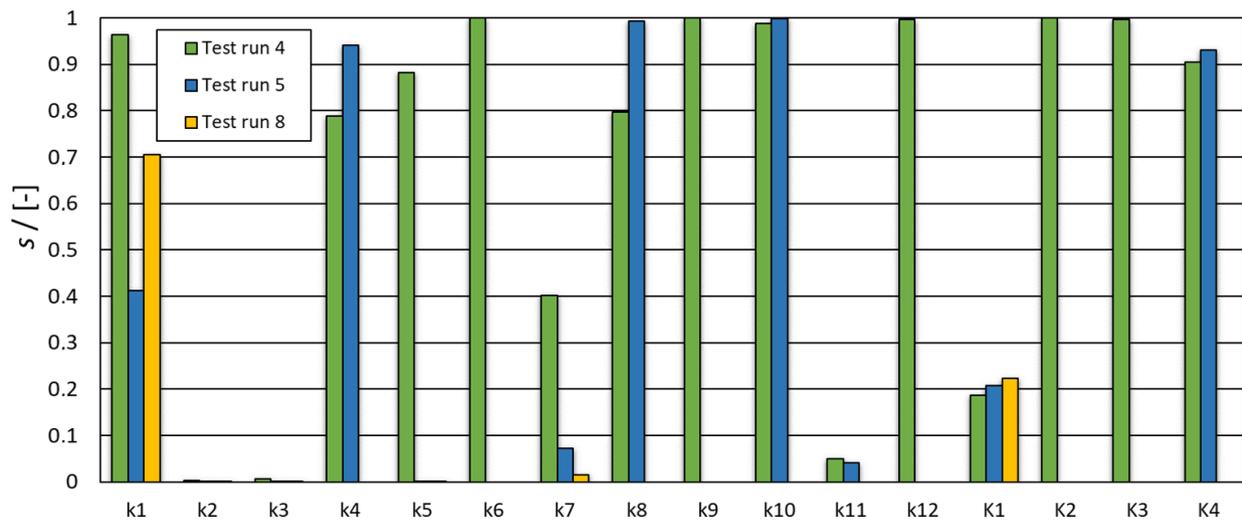


Figure 8. Parameter intervals for model (1) according to Langmuir-Hinshelwood.

Table 3. Solution results of the inverse kinetic task determined for the model according to the Langmuir-Hinshelwood mechanism at $P_1 = 220, P_2 = 500, P_3 = 5$.

Solution Interval	Determined Numerical Values for the Model Parameters k and n	Equation Nr.	RSS
Test run 1			
$k'_i \in [0,1], K_i \in [0,1]$	$k_1 = 0.999, k_2 = 0.256, k_3 = 0.0000, k_4 = 0.999, k_5 = 0.0233, k_6 = 0.999, k_7 = 0.999, k_8 = 0.0000, k_9 = 0.300, k_{10} = 0.999, k_{11} = 0.999, k_{12} = 0.655, K_1 = 0.999, K_2 = 0.0000, K_3 = 0.999, K_4 = 0.999$	(1)	2.8512
Test run 2			
$k'_i \in [0,5], K_i \in [0,5]$	$k_1 = 4.999, k_2 = 0.832, k_3 = 0.0004, k_4 = 0.0937, k_5 = 0.0283, k_6 = 4.999, k_7 = 2.891, k_8 = 4.999, k_9 = 0.140, k_{10} = 0.0003, k_{11} = 1.124, k_{12} = 0.004, K_1 = 4.999, K_2 = 1.559, K_3 = 2.008, K_4 = 4.999$	(1)	0.1056
Test run 3			
$k'_i \in [0,10], K_i \in [0,10]$	$k_1 = 9.999, k_2 = 0.00000118, k_3 = 0.188, k_4 = 0.702, k_5 = 0.259, k_6 = 9.999, k_7 = 5.441, k_8 = 9.999, k_9 = 0.0598, k_{10} = 1.100, k_{11} = 1.502, k_{12} = 0.000006, K_1 = 4.238, K_2 = 9.999, K_3 = 9.997, K_4 = 7.701$	(1)	0.0177
Test run 4			
$k'_i \in [0,100], K_i \in [0,100]$	$k_1 = 20.819, k_2 = 0.00018, k_3 = 0.0146, k_4 = 14.641, k_5 = 0.0354, k_6 = 39.731, k_7 = 3.633, k_8 = 0.095, k_9 = 75.125, k_{10} = 47.151, k_{11} = 1.739, k_{12} = 65.005, K_1 = 10.942, K_2 = 92.385, K_3 = 0.0003, K_4 = 2.752$	(1)	7.965×10^{-4}
Test run 5			
$k'_i \in [0,100], K_i \in [0,100]$	$k_1 = 40.708, k_2 = 0.0002, k_3 = 0.0057, k_4 = 0.1396, k_5 = 0.0336, k_7 = 7.136, k_8 = 0.6578, k_{10} = 1.1538, k_{11} = 2.7629, K_1 = 2.403, K_4 = 58.04589$	(5)	9.6711×10^{-4}
Test run 6			
$k'_i \in [0,100], K_i \in [0,100]$	$k_1 = 91.235, k_2 = 5.632 \cdot 10^{-7}, k_3 = 2.795 \cdot 10^{-8}, k_5 = 0.015, k_7 = 12.094, k_{10} = 0.636, k_{11} = 7.234, K_1 = 1.016, K_4 = 99.994$	(5)	9.7681×10^{-4}
Test run 7			
$k'_i \in [0,100], K_i \in [0,100]$	$k_1 = 19.262, k_2 = 0.039, k_3 = 1.109 \cdot 10^{-8}, k_5 = 6.465 \times 10^{-9}, k_7 = 0.332, k_{10} = 67.251, K_1 = 13.854$	(5)	0.0166
Test run 8			
$k'_i \in [0,100], K_i \in [0,100]$	$k_1 = 19.272, k_2 = 0.0392, k_3 = 1.364 \cdot 10^{-10}, k_5 = 3.808 \times 10^{-9}, k_7 = 0.332, K_1 = 13.782$	(5)	0.0166

The parameter values obtained using the model approach according to (5) and the corresponding parameter value ranges are summarized in Table 3 and Figures 7 and 8. As shown in Figures 7 and 8 for the 5th test run, the rate constants k_4 and k_8 have only a very small influence on the overall result and can therefore be excluded in the 6th test run. After the 6th test run, the model structure can be simplified consequently up to six parameters: $k_1, k_2, k_3, k_5, k_7, K_1$ (Table 3, 8th test run). However, after model simplification, the RSS increased from 9.6711×10^{-4} to 0.0166.

Table 4 summarizes the results of the model evaluation of the hydrogenation of cinnamic aldehyde according to the Langmuir-Hinshelwood approach. This analysis confirms that the model 8, obtained in the 8th test run, is characterized by the lowest number of model parameters and the best values of the evaluation criteria: $AIC = \min, AIC_c = \min, \Delta_i = \Delta_{\min} \rightarrow 0$. Models 1 to 5, for which $\Delta_i > 10$, cannot represent the experimental dependencies in the required way. For these models: $\omega_1 = \omega_2 = \omega_3 = \omega_4 \approx \omega_4 \approx 0$. The weights of models 6, 7, and 8, calculated according to (17), are: $\omega_6 = 0.0230, \omega_7 = 0.1779, \omega_8 = 0.7985$. The weight ratios ω_3/ω_j , which indicate how much the respective model contributes to the overall prediction, are $\omega_8/\omega_6 = 34.73$ und $\omega_8/\omega_7 = 4.49$.

Table 4. Evaluation of model quality based on information criteria for the mathematical description of cinnamic aldehyde hydrogenation according to the Langmuir-Hinshelwood approach.

Model-No.	Test Run	F^2	$\log((L(\hat{k}, \hat{\sigma}^2 Daten))$	N	AIC	AIC_c	$\Delta_i AIC_c$	ω_i
1	1	2.8512	26.15	17	31.62	55.16	44.90	0.0000
2	2	0.1056	57.64	17	28.76	52.30	42.03	0.0000
3	3	0.0177	74.70	17	27.21	50.75	40.48	0.0000
4	4	7.965×10^{-4}	104.33	17	24.52	48.05	37.79	0.0000
5	5	9.6711×10^{-4}	102.48	12	14.68	24.75	14.48	0.0006
6	6	9.7681×10^{-4}	102.38	10	10.69	17.36	7.09	0.0230
7	7	0.0166	75.31	8	9.15	13.27	3.00	0.1779
8	8	0.0166	75.31	7	7.15	10.26	0.00	0.7985

This confirms that model 8 is best suited for the redundancy-free description of the hydrogenation of cinnamic aldehyde based on the Langmuir-Hinshelwood mechanism. The kinetic reaction scheme based on this mechanism is shown in Figure 9. The advantage of model 8 over model 7 is achieved by reducing the number of model parameters and thus simplifying the complexity of the reaction system without changing the sum of squares of errors.

The best formulated redundancy-free models for the hydrogenation reaction based on the formal-kinetic (formal kinetic model 7 (2nd test run) in Table 2) and the Langmuir-Hinshelwood approach (Table 2 and the model 8 (8th test run) are to be compared in terms of their quality and significance. The value of the error square sum of $RSS = 0.0648$ was determined for the first model and of $RSS = 0.0166$ for the second model. It means that the model based on the Langmuir-Hinshelwood theory reflects the experimental results better compared to the model based on the formal kinetic approach. On the other hand, it contains 6 model parameters, while the formal kinetic model has only 4 parameters. In contrast, the values of the Akaike criterion for the Langmuir-Hinshelwood model approach are $AIC = 7.15$ and for the formal kinetic approach $AIC = 4.34$.

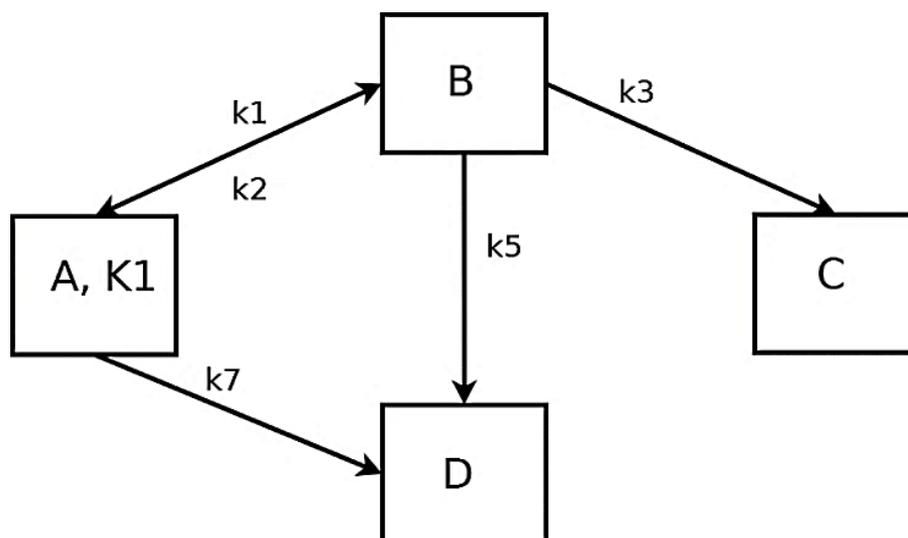


Figure 9. The simplified, redundancy-free model of the cinnamic aldehyde hydrogenation according to the Langmuir-Hinshelwood approach based on data from Table 4, 8th test run.

The simplification achieved in the redundancy-free model based on the Langmuir-Hinshelwood approach can be explained by the fact that, in the case of significant adsorption of the starting molecules in the catalyst surface, the degrees of freedom of adsorbed molecules decrease, which reduces their reactivity. In this way, three degrees of freedom of molecular rotation in the gas phase are reduced to one degree of freedom for the adsorbed molecules. The same is characteristic for the degrees of freedom of molecular rotation, the number of which decreases from three in the gas phase to two in the adsorbed state. Consequently, the probability of the direct conversion of cinnamic aldehyde (A) to 3-phenylpropanol (C) according to the redundancy-free model in Figure 9 is practically negligible compared to the model in Figure 6c

3. Materials and Methods

Two different modelling ways were used to describe the three-phase catalytic hydrogenation of cinnamaldehyde: formal kinetics and kinetics concerning the Langmuir-Hinshelwood theory in the mechanism of heterogeneously catalyzed reaction [11].

The introduced approach is based on an automatically created redundant (generalized) model, which is formulated according to the complete reaction network—GD (Figure 2) [10].

There are six main steps to obtain the redundancy-free model (Figure 10) [9]. These steps can be used several times depending on a one-step simplification strategy or step-by-step simplification strategy [10]. For the hydrogenation of cinnamic aldehyde, only step-by-step simplification was applied. The aim of the model simplification is to obtain such a model, which provides minimal difference between the outputs of the redundant and simplified model:

$$\min |C - C'| \quad (6)$$

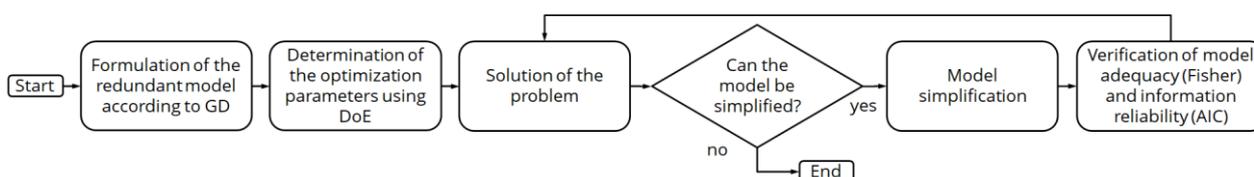


Figure 10. Model simplification route.

With conditions

$$C = \sum v \cdot r(k, n), \quad C(0) = C_0, \quad (7)$$

$$C' = \sum v \cdot R \cdot r(k', n'), \quad C'(0) = C_0, \quad (8)$$

$$\sum_{i=1}^N R_i = m, \quad \text{with } R_i = 0 \text{ or } 1 \quad (9)$$

where v is the matrix of stoichiometric coefficients, r , k , C , n are reaction rate, rate constant, concentration and reaction order vectors, R is a matrix with elements equal to 0 or 1, k' , C' , n' are rate constants, concentrations and reaction order vectors, for the redundancy-free model, N is the number of equations in the redundant model; m is the number of equations in the simplified (redundant-free) model.

The formal kinetic model is based on the rate law. The reaction rate is assumed proportional to the rate constant k and concentration C of the reaction components:

$$\frac{1}{v_i} \frac{dC_i}{dt} = r_j = k_j \prod_i C_i^{n_i}, \quad (10)$$

where n_i is the reaction order of the component i .

In addition to the formal kinetic approach, the procedure according to Langmuir-Hinshelwood also plays an important role in the heterogeneously catalyzed hydrogenation of cinnamic aldehyde. The assumptions of the Langmuir-Hinshelwood mechanism are to be considered:

- Adsorption of organic molecules on the catalyst surface occurs according to Langmuir;
- Hydrogen adsorption does not compete with the adsorption of organic molecules;
- Surface reaction is the rate-determining step;
- Organic molecules are irreversibly hydrogenated;
- Hydrogenation takes place at the so-called active site (single-site model).

As experimental investigations of the three-phase catalytic hydrogenation of cinnamic aldehyde were carried out at constant pressure, it was assumed that the degree of coverage of the active catalyst surface with hydrogen always remains constant during the experiment. This degree of coverage was included in the equation for determining the corresponding rate constant: $k'_i = k_i \cdot \theta_H$, where θ_H —is the degree of surface coverage with hydrogen. The formulated system of differential equations (10) can also be solved under the assumption of the Langmuir-Hinshelwood mechanism, whereby the rate of every reaction stage is defined by the following equation:

$$r_j = \frac{k'_i C_i K_i}{1 + \sum_{i=1}^M C_i K_i}, \quad (11)$$

It is assumed that the reaction order is equal 1, and a new parameter, the adsorption constant K_j , is introduced.

In the first step, concerning Equations (10) and (11) a vector-type GD, the (redundant) model is formulated. In the second step, the optimization parameters for the formulated system are determined based on design of experiments (DoE). A fine-tuned minimization of the variance between experimental and simulation data is provided for parameter estimation. In the next step, the solution of the problem is estimated. Starting points are generated using uniformly distributed random numbers to provide a global solution of parameter determination by the downhill simplex method. This procedure is repeated several times according to the optimization parameters defined at the previous stage. The

algorithm works in the parameter definition area. At each optimization step, the objective function RSS (Residual Sum of Squares) is calculated:

$$RSS = \sum_{i=1}^N \sum_{j=1}^M [C_{ij} - \overline{C}_{ij}(k)]^2, \quad (12)$$

where C_{ij} are the experimental concentration values, and $\overline{C}_{ij}(k)$ are according to model calculated values.

Based on the contribution of a parameter to the final value of the objective function, it is possible to make a statement about its relevance and redundancy freedom. Thus, this simple procedure can also be applied for the evaluation of parameter relevance in the models of complex chemical reactions. In the approach, the uncertainty is defined in the form of an interval in which the parameter changes take place during its determination from different starting points. These parameters have low contribution to the objective function. Therefore, these determined parameter have almost no influence on the model output and can be eliminated at every elimination step. Simultaneously, sensitivity analysis is performed to determine normalized model parameter values and their intervals and to identify the model parameters that have the greatest influence on the model output. Local or global methods of sensitivity analysis can be used for this procedure [12]. Based on the results, model simplification is provided. If the model can be simplified, a new model is formulated, which is then verified by statistical tests, i.e., the Fisher test (F -test), and the Akaike information criterion (AIC).

The information-theoretic approach allows the data-based selection of the “best” model and a ranking of the remaining models in a pre-defined set. Using the Akaike criterion, the Kullback-Leibler discrimination information can be estimated based on the empirical log-likelihood function at its maximum point [13,14]:

$$L = \log\left((L(\hat{N}, \hat{\sigma}^2 | \text{data}))\right) = -\frac{n}{2} \cdot \log(\hat{\sigma}^2), \quad (13)$$

where $\hat{\sigma}^2$ —consistent estimation (maximum likelihood method) of the variance of the model random error; L —the value of the log likelihood function for the model; n —the sample size. This can be determined according to the following equation:

$$AIC = 2N - 2L. \quad (14)$$

where N —number of parameters, the Akaike criterion indicates that the experimentally determined kinetic relationships are not informative enough. For such cases, Sugiura suggested model comparisons according to the modified Akaike criterion [15,16]:

$$AIC_c = AIC + [2N(N + 1)] / (n - N - 1), \quad (15)$$

Since the values of the AIC criterion can be compared only with each other, the analysis uses the criteria difference Δ_i . The larger the numerical value of Δ_i is, the less probability is given that the model $f(x)_i$ is the best of all considered models:

$$\Delta_i AIC_i = AIC_i - AIC_{min}. \quad (16)$$

To simplify the discussion about the model’s information reliability, so-called Akaike weights for R models are introduced [17]:

$$\omega_i = \exp(-0,5\Delta_i) / \left[\sum_{r=1}^R \exp(-0,5\Delta_r) \right]. \quad (17)$$

After this step, the new model is to be checked in order to find if further simplification is possible. If further simplification is not possible, the redundancy-free model is obtained.

4. Conclusions

An approach for redundancy-free model description of the three-phase catalytic hydrogenation of cinnamaldehyde is introduced. Two different modelling ways were investigated and analyzed: formal kinetics and kinetics concerning the Langmuir-Hinshelwood mechanism. The redundancy-free model formulation procedure consists of six steps, which are used several times in a step-by-step simplification strategy.

Model 7 based on formal kinetics (2nd test run) with $RSS = 0.0648$ and model 8 (8th test run) based on the Langmuir-Hinshelwood mechanism with $RSS = 0.0166$ were obtained. The model based on the Langmuir-Hinshelwood approach seems to reflect the experimental results better compared to the formal kinetic approach. On the other hand, it contains 6 model parameters, while the formal kinetic model has 4 parameters. The values of the Akaike criterion for the Langmuir-Hinshelwood model approach are $AIC = 7.15$ and for the formal kinetic approach $AIC = 4.34$.

Significant adsorption of the starting molecules on the catalyst surface degrades the freedom of the adsorbed molecules, reducing their reactivity in the redundancy-free model based on the Langmuir-Hinshelwood approach. In this way, three degrees of freedom of molecular rotation in the gas phase are reduced to one degree of freedom for adsorbed molecules. The degrees of freedom of molecular rotation decrease from three in the gas phase to two in the adsorbed state. Therefore, the probability of a direct conversion of cinnamic aldehyde (A) to 3-phenylpropanol (C) according to the redundancy-free model based on Langmuir-Hinshelwood approach in Figure 9 is practically negligible compared to the model based on formal kinetics Figure 6c.

The provided models are based on the assumption that the redundancy-free reaction model is obtained more or less automatically and therefore fast. It was shown that the formulation of the mathematical description of detailed chemical kinetics for the simplest boundary conditions without physical transport is possible without great effort. The approach was also tested for other reaction systems. Therefore, the proposed approach could also be of interest in industrial practice.

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