

Methane steam reforming unraveled by the MicroKinetic Engine, a user-friendly kinetic modeling tool

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Kinetic modeling forms the bridge between the phenomena occurring at the molecular and reactor scale. It results in a mathematical representation of the underlying reaction network and mechanism. The comparison between experimental observations and model simulations allows a critical evaluation of the assumptions made during model construction. This turns kinetic modeling into an important activity in chemical engineering. Moreover, the resulting models provide strategic information aiming at the optimization and intensification of industrial chemical reactors, and even entire processes. From an industrial point of view, global kinetic models such as power law or Langmuir-Hinshelwood-Hougen-Watson (LHHW) models often provide sufficient information for process control and optimization. However, narrowing margins and increasing computational capabilities open up perspectives for more fundamental kinetic modeling, which, up to recently, was only exploited by academia. In addition, the shift towards green production processes underlines the need for a more detailed understanding of the more complex nature of biomass conversion.

A broad spectrum of dedicated software tools with various features is available to construct such (micro)kinetic models. However, there is a significant induction period for novices in the field of kinetic modeling to get acquainted with the methodology, since a good, boundary-crossing knowledge between chemistry, mathematics, statistics and (chemo)informatics is required. In order to make fundamental kinetic modeling more accessible as well as to reduce the time spent for model construction, a user-friendly tool has been developed: the MicroKinetic Engine (μ KE).

MicroKinetic Engine (μ KE)

The μ KE is a software package for the simulation and regression of chemical kinetics and even non-chemical applications such as solar cells characteristics simulation have been demonstrated with this tool. It has been developed during the last decade at the Laboratory for Chemical Technology, Ghent University, Belgium and was originally constructed for the detailed kinetic modeling of heterogeneously catalyzed reactions. In order to simulate different reactor types, both differential and algebraic equation solvers have been integrated in the software library. To enable model regression to experimental data, two deterministic regression routines are included, i.e., the Rosenbrock [1] and Levenberg-Marquardt algorithm [2]. A Graphical User Interface (GUI), see Figure 1 (left), is wrapped around all these routines such that no programming effort whatsoever is required from the μ KE user, making it very distinct from other chemical modeling tools such as Athena Visual Studio (<http://www.athenavisual.com/>) or Chemkin (<http://www.reactiondesign.com/products/chemkin/chemkin-2/>).

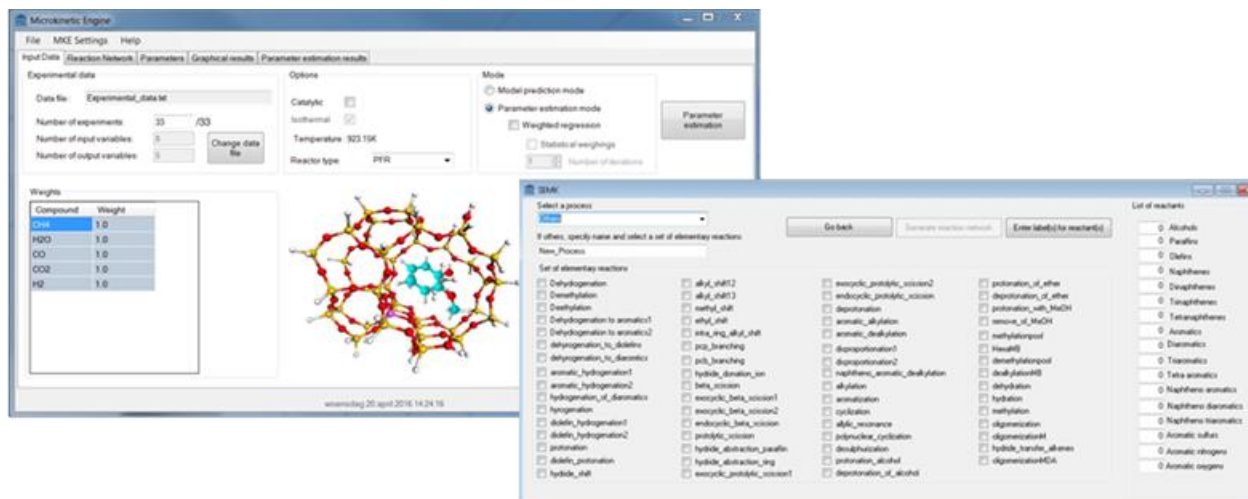


Figure 1. Graphical User Interface of the MicroKinetic Engine. Left: window for problem definitions, right: window for automatic network generation

The μ KE consists of an onion structure as indicated in Figure 2. At its core, the μ KE has the kinetic model which expresses the reaction rates of every (elementary) step included in the network. By default, the law of mass action is applied to calculate the corresponding rates, but also power laws or user defined functions can be included. Due to the latter, also applications other than chemical kinetics can be handled by the μ KE, for example simulating a light-generated current as a function of the solar cell properties and the applied voltage. These rate equations are subsequently incorporated in a reactor model which describes the mass balance of all components over the selected reactor type. The corresponding set of algebraic and/or differential equations is solved using DASPK3.0 (<https://techtransfer.universityofcalifornia.edu/NCD/10326.html>) in order to calculate the individual outlet flow rates. If regression is required, an additional shell is activated in which the Rosenbrock method performs a first estimation effort, after which the Levenberg-Marquardt algorithm takes over to further optimize the parameter estimates. Both regression algorithms are based on the minimization of the (weighted) residual sum of squares of the responses in order to determine optimal parameter estimates.

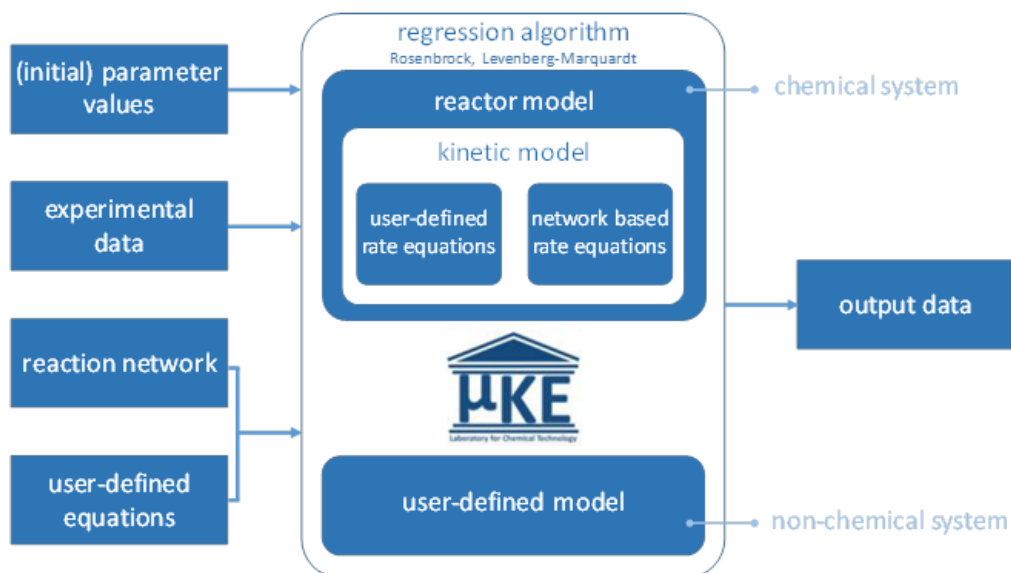


Figure 2. Structure of the MicroKinetic Engine

The input of the μ KE comprises (initial) parameter values, experimental data, including independent and dependent variables (also denoted as ‘operating conditions’ and ‘responses’), and the proposed reaction network for chemical kinetics. The reaction network can be constructed either manually via the GUI, or automatically thanks to the integration with the Reaction Network Generator (ReNGeP) [3] or, by extension, by any other network generation program, see Figure 1 (right). The μ KE automatically converts the reaction network into the corresponding rate equations which are subsequently called from the reactor model. Instead of a reaction network, user-defined equations can be given which are applicable to both chemical and non-chemical systems. The output of the optimization procedure consists of the model simulations and, in case of regression, an extended statistical analysis and the corresponding optimal parameter estimates. In case of reversible steps, the parameter estimates are determined such that thermodynamic consistency is assured for each of the reaction steps. Additionally, the μ KE identifies quasi-equilibrated reaction steps while no assumptions have to be made *a priori* on rate-determining step(s) or quasi-equilibria. If required, a rate of production analysis is performed by the μ KE providing an additional layer of insight in the reaction network included.

Methane steam reforming

To demonstrate the features and versatility of the μ KE, methane steam reforming is selected as a case study. To model the reaction mechanism of this industrially relevant process, a model is proposed with increasing complexity, i.e., going from a global power law model towards a LHHW type model.

The model is regressed to the experimental data acquired by Kageyama et al. [4]. The dataset comprises 80 experiments, performed in a tubular packed bed reactor at a total pressure of 0.4 MPa in a temperature range from 893 to 943 K with space times ranging from 0.96 to 3.36 kg s mol⁻¹ and CH₄ to H₂O molar ratios between 0.125 and 0.7. In some experiments, CO, CO₂ and/or H₂ were added to the feed. The catalyst is an industrial SiO₂-MgO supported Ni catalyst.

The three reaction networks, i.e., corresponding to a power law model, a model with reactants adsorption and a Langmuir-Hinshelwood model, used for the kinetic model are shown in Figure 3. The adsorption/desorption steps in the latter two models are assumed to be in quasi-equilibrium. To reduce the number of parameters in the Langmuir-Hinshelwood model and based on literature, it is assumed that the adsorption equilibrium coefficient of methane and water are equal to $0.15K_{5C}$ and $0.05K_{5C}$ respectively, with K_{5C} the adsorption equilibrium coefficient of CO, and that CO₂ leaves the catalyst surface instantaneously ($K_{6C} = 0$), see Table 1 in bold. Moreover, the partial reaction order of hydrogen in the reforming step is set to one instead of three, as this clearly concerns a non-elementary step. The weighted regression of each model to the experimental data was found to be globally significant with statistically significant parameter estimates, see Table 1.

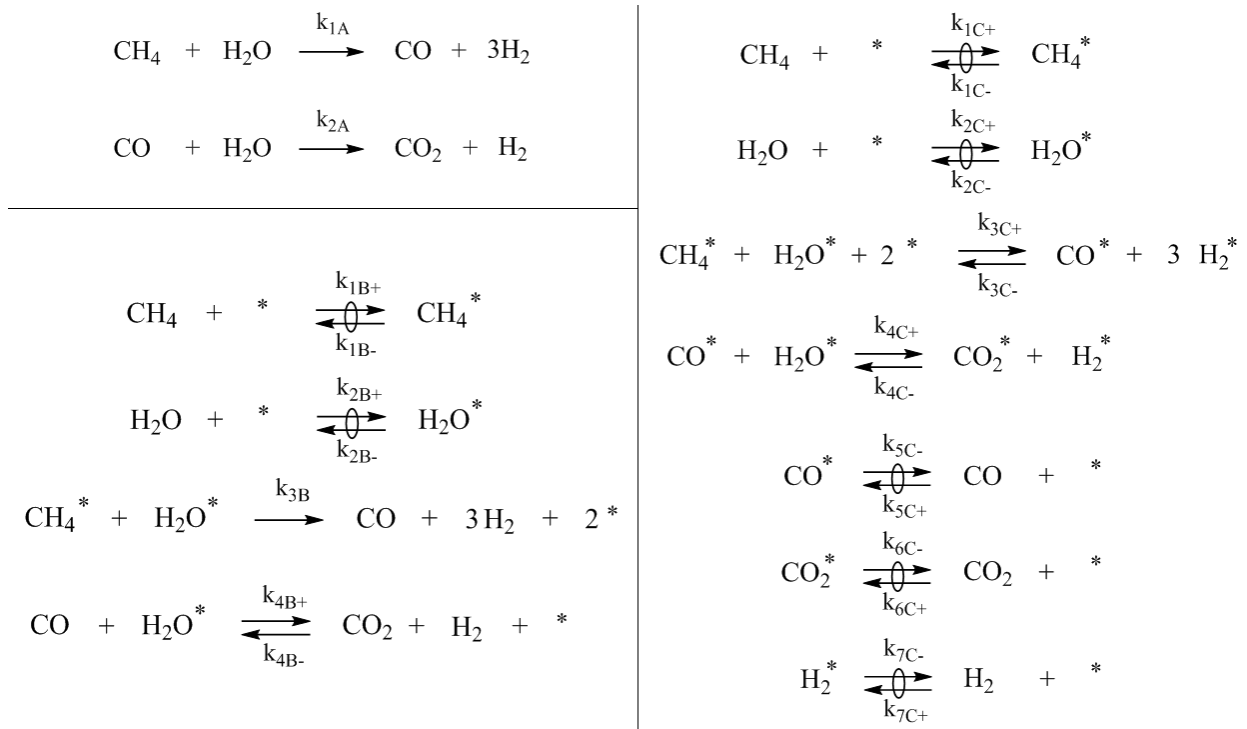


Figure 3. Reaction network for the Langmuir-Hinshelwood kinetic model for methane steam reforming. Left, up: power law model; left, down: model with reactants adsorption; right: Langmuir-Hinshelwood model

Table 1. 95% confidence interval of the model parameters of the power law model (left), the model with reactants adsorption (middle) and the Langmuir-Hinshelwood model (right).

power law model			model with reactants adsorption			Langmuir-Hinshelwood model			
	95 % confidence interval	units		95 % confidence interval	units		95% confidence interval	units	
k_{1A}	1.76 ± 0.34	$10^{-3} \text{ mol s}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ Pa}^{-0.44}$	K_{1B}	28.8 ± 4.8	MPa^{-1}	K_{1C}	0.15	K_{5C}	MPa^{-1}
k_{2A}	1.89 ± 1.34	$10^{-5} \text{ mol s}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ Pa}^{-0.91}$	K_{2B}	12.5 ± 2.3	MPa^{-1}	K_{2C}	0.05	K_{5C}	MPa^{-1}
p_{1,CH_4}	0.36 ± 0.05	-	k_{3B}'	1.63 ± 0.12	$\text{mol s}^{-1} \text{ kg}_{\text{cat}}^{-1}$	k_{3C+}'	267 ± 238		$\text{mol s}^{-1} \text{ kg}_{\text{cat}}^{-1}$
$p_{1,\text{H}_2\text{O}}$	0.081 ± 0.078	-	k_{4B+}'	1.11 ± 0.03	$10^{10} \text{ mol s}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ MPa}^{-1}$	k_{4C+}'	1.39 ± 0.34		$10^{10} \text{ mol s}^{-1} \text{ kg}_{\text{cat}}^{-1}$
$p_{2,\text{CO}}$	0.50 ± 0.13	-				K_{5C}	23.2 ± 19.6		MPa^{-1}
$p_{2,\text{H}_2\text{O}}$	0.41 ± 0.10	-				K_{6C}	0		MPa^{-1}
						K_{7C}	14.7 ± 11.6		MPa^{-1}

As expected the power law model exhibited a poor performance, see Figure 4, which is attributed to the lack of reactant and product interaction with the catalyst that was accounted for. By only taking reactant adsorption and the reversibility of the water-gas shift reaction into account, the model performance improved significantly, yielding an acceptable performance combined with a clear physical meaning of the model parameter estimates. The model performance did not further significantly improve by taking product adsorption into account, indicating that the model has become overparametrized and/or insufficient information is available in the dataset.

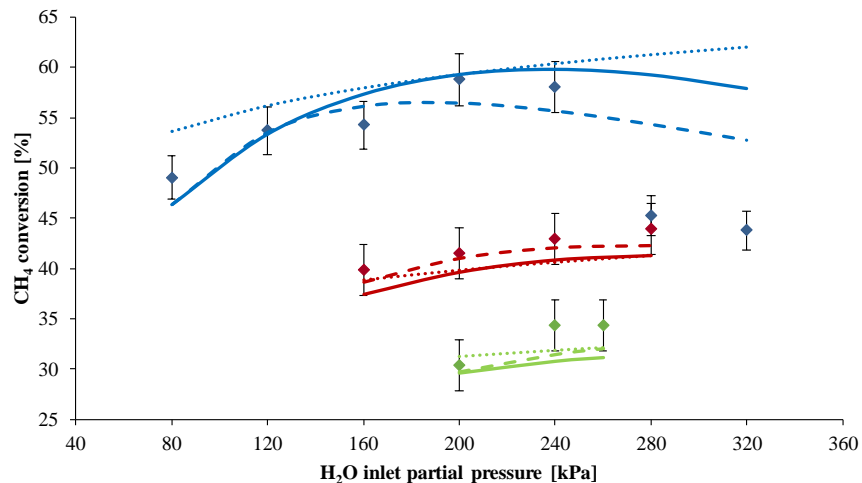


Figure 4. Methane conversion as a function of the water inlet pressure at a total pressure of 0.4 MPa and a temperature of 923 K. Symbols: experimentally observed with (blue) 40 kPa inlet partial pressure of CH_4 ($p_{\text{CH}_4,\text{in}}$) and a space time of $3.36 \text{ kg}_{\text{cat}} \text{ s mol}_{\text{CH}_4}^{-1}$, (red) 80 kPa $p_{\text{CH}_4,\text{in}}$ and a space time of $1.68 \text{ kg}_{\text{cat}} \text{ s mol}_{\text{CH}_4}^{-1}$, (green) 120 kPa $p_{\text{CH}_4,\text{in}}$ and a space time of $1.12 \text{ kg}_{\text{cat}} \text{ s mol}_{\text{CH}_4}^{-1}$, lines: simulated via weighted regression. Dotted line: power law model, dashed line: model with reactants adsorption, full line: Langmuir-Hinshelwood model.

Conclusion

Through the case study of methane steam reforming, the μ KE has proved to be a well performing and strongly user-friendly software package for the simulation and regression of chemical kinetics. With minor user intervention, regressions could be performed providing, in an automated manner, the statistical interpretation of these results, such that the user can focus on their physical interpretation. The gradual expansion of the model complexity for methane steam reforming has indicated that the most important phenomena to describe our dataset are the adsorption of the reactants and the reversibility of the water-gas shift reaction.

References

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