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Qualitative Analysis Based Reaction Mechanism Identification

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One of the most important tasks during the design process of a chemical technology is the engineering design of the conversion subsystem based on the aspect of optimal and safe operation. Hence, before the design the rate of processes which have impact on the dynamic behaviour of the subsystem must be identified. The reaction mechanism of a reaction system represents all the elementary reaction steps which are required to convert the reagents into products. The aim of the reaction mechanism analysis is the identification of the route how the system goes from its initial to the end state.
The developed tool can be applied to identify unknown reaction mechanism without the necessary chemist experience based. Beside, the tool can be used to determine the parameters of the rate equations of each identified chemical reaction. The first task requires the application of structure while the second one requires parameter identification methods. The developed structure identification method is based on qualitative trend analysis of measured and calculated state-variables trajectories, since the trends in the change of components can be easily compared based on the resulted sequences. To solve the constraint optimization problem during the parameter identification process an improved evolutionary strategy method is applied.

1. Introduction

One of the most important tasks during the design process of a chemical technology is the engineering design of the conversion subsystem based on the aspect of optimal and safe operation. Hence, before the design phase the processes which have impact on the dynamic behaviour of the subsystem and their rate must be identified. The most crucial part of the conversion subsystem is the chemical reactor in which we try to control the processes based on the knowledge gained in laboratory experiments. These can be physical, chemical or physicochemical processes. In this work I proposed a method to support the recognition of chemical processes which take place in reactors.
Many books and articles can be found which show different methodologies to identify reaction mechanisms – e.g. a general one by Delvin (2002) and a guide handbook (Grossman, 2003). Thermogravimetry using geometric analysis (Haixiang et al., 2010) and kinetic studies (Lee and Dollimore, 1998), and combined online-Raman-spectroscopy with offline nuclear magnetic resonance (Litzmann et al., 2012) measurements can be applied in reaction identification process without modelling the system. Searson et al. (2006) proposed a method based on the general model of a batch reactor, which consists all the reaction rates for all the possible reactions and using parameter estimation to determine which part of the equations has the biggest impact on the concentration trajectories. Integer linear optimization is another useful tool in reaction mechanism identification based on the molecular structure of the species (First et al., 2012). As we know more and more about reactions and have more and more computational capacities we can investigate complex reaction systems to support the design of chemical reactors.
The reaction mechanism of a reaction system represents all the elementary reaction steps which are required to convert the reagents into products. Hence, the aim of reaction mechanism identification is the determination of the intermediate steps which require to obtain the final product. Of course, we are far from that we can follow and model the movement of all molecules in a system in detail. However, we can give

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that a picture about a reaction system based on the cumulative effect of great number of molecules in specific states. Such specific states are the formation of relatively stable intermediates.
The intermediates are those chemical species produced in the elementary reaction steps which can be detected with any of the possible measurement methods. The produced amount of these intermediates is very low sometimes and they react very fast to produce another intermediate or final product. Hence, the identification of these components and the measurement of their concentrations can be very difficult. Most of the reactions take place through many intermediate steps. Hence, these are called multi step reactions which are the series of element reaction steps. In a single reaction step the sign of stoichiometric coefficients represent that a given molecule is a reagent (-) or a product (+) in that step. The absolute value of these coefficients gives how many moles have been consumed/formed.
The transient states of a reaction system and the intermediates can be investigated two ways, which are based on reaction kinetic and which are not (Friess, 1963). The foundation of the reaction mechanism analysis is the precise identification of all intermediates and their concentration. Without of this information the stoichiometric of the reaction cannot be reliable determined. The nature and the amount of the products can contain as much information as a well qualified chemist requires identifying the reaction mechanism of an unknown reaction system. The proposed tool can support this process in case the experience is lacking in the identification of reaction mechanism and/or the parameters of kinetic expressions.
The essence of the parameter identification process is the solution of a constrained minimization problem in which the objective function can be the summarized square error between the measured and the calculated component profiles and the searching variables are the unknown parameters of the kinetic expressions. To solve the constrained minimization problem in the parameter identification step an improved evolutionary strategy algorithm is applied (Hansen, 2000).
The role of the structure identification is the identification of the correlated variables and the mathematical formalization of these correlations. In our case it means the identification of reactions which take place in the reactor. The applied structure identification method is based on qualitative trend analysis because using this technique the trends in measured and in calculated profiles can be easily compared. The simplest primitive episode pool (i.e. which consists the fewest episodes) has been determined in (Cheung and Stephanopoulos, 1990). These episodes are obtained based on the sign of first and second derivatives of the given time series. Seven primitive episodes can be differentiated as it can be seen in Figure 1.

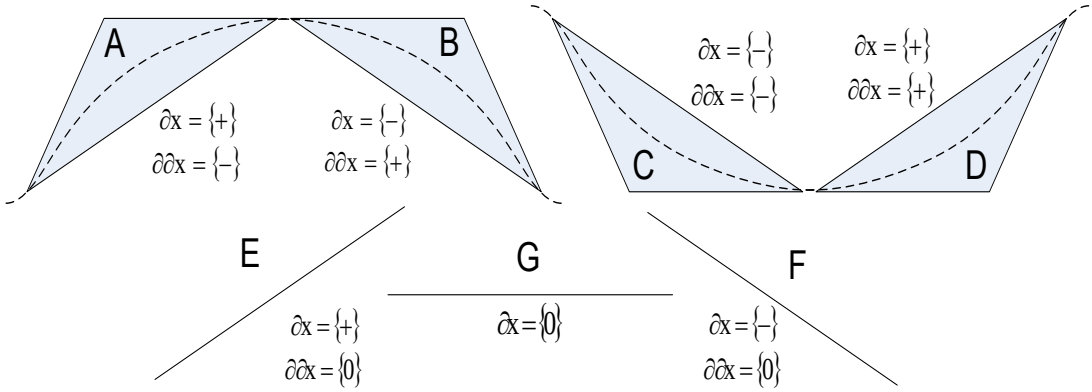

Figure 1: Primitive episodes

If the analyzed time series are not independent from each other then the resulted sequences can contain information about the structure of the system. Just imagine that the investigated time series are obtained in reaction kinetic experiment. In this case these time series can be the results of some kind of composition, pressure or temperature (or calorimetric) measurements collected during the experiment. Necessarily, these time series are strictly connected to each other. Applying qualitative trend analysis in this case the trends can be identified which represents a reaction, e.g. in a simple case the concentration of two components decreases while the concentration of a third component increases. We can identify a reaction which connects these three components in which the first two components are reagents while the third one is the product. In a real reaction system usually there are multiple reactions which take place at the same time so the identification of reaction steps is more difficult without the development of mathematical models.

2. The proposed algorithm

The aim of this work is to develop a tool which can support the reaction mechanism identification process of unknown reaction systems and based on the revealed or supposed reaction mechanism it can be applied to identify the reaction kinetic parameters. The first step in the development is the design of the algorithm for reaction mechanism identification (see in Figure 2). The first step of the developed algorithm is the processing of the measured data which can be the earlier mentioned time series. In this phase of the development only the concentration measurements can be loaded. During the data processing each of the time series is transformed into the sequence of primitive episodes based on qualitative trend analysis. The result of this data processing step is the fingerprint of the reaction mechanism behind the investigated reaction system which is the sequence for all components measured during the experiment.

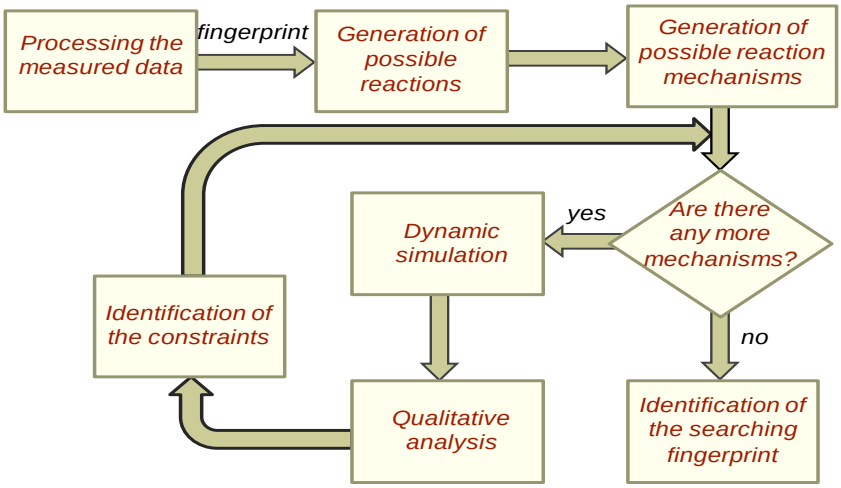

Figure 2: The proposed algorithm for reaction mechanism identification

To generate the possible reaction steps all the assumed components must be added to the component list. Not measured components can also be added to this list. Based on the formula and molecular mass the possible reaction steps, which can be part of the unknown reaction mechanism can be determined. In that case if we identify all the independent reaction steps from the reaction list we obtain a narrower reaction list, which contains only the basic reaction steps. The independent reactions are those reactions which cannot be produced by any linear combination of the other reactions.

In the next step of the algorithm all the possible reaction mechanisms are generated based on the reaction steps in the pruned reaction list. The possible reaction mechanism can be filtered based on some *a prior* information, e.g. if we see from the measured data that the concentration of component A is decreased in specified time segments of the experiment, then all the reaction mechanisms, in which there is not at least one reaction which consumes component A, can be deleted. One of the reaction mechanisms in the resulted list is the one we are looking for to find the perfect match. Hence, all these mechanisms must be "interrogated". It means a dynamic reactor simulator must be developed for all these mechanisms and checked what kind of fingerprints the mechanisms can produce.

The kinetic experiments are usually performed in a flask which can be approached as a batch reactor. All the reagents are added to the unit with or without a catalyst. Samples are taken from the reaction mixture after specific time. There are much more sophisticated apparatus is required for kinetic experiments in which heat produced by the reactions, the pressure and/or the temperature of the reaction mixture can be measured too. As it is mentioned earlier the simplest case is considered as we have only concentration measurements from a batch reactor. However, the developed tool can be improved and the processable data can be widened with the application of mathematical models of other reactor types.

As we need the model of a batch reactor the component mass balance equations can be simplified and obtained the next expression:

$$\frac{dc_i}{dt} = R_i \qquad i = \{A;B;C;..\}, \tag{1}$$

where c_i is the concentration of the i^{th} component [mol/dm^3]; R_i is the component source of the i^{th} component [mol/dm^{3}s], which can be calculated as:

$$R_i = \sum_{j=1}^{n} \upsilon_{ij} \cdot r_j \,, \tag{2}$$

where j represents the number of the reaction; v_{ij} is the stoichiometric coefficient of the ith component in the jth reaction [-]; r_j is the reaction rate of the jth reaction [mol/dm^{3}s], which is calculated with following expression:

$$r_j = k_j \prod_{i=\{A;B;C;\ldots\}} c_i^{n_{ij}} \,, \tag{3}$$

where k_j is the reaction rate constant of the jth reaction [the unit is dependent on the order of the reaction]; n_{ij} is equal of the absolute value of the stoichiometric coefficient of the ith component in jth reaction if this component is reagent in that reaction, otherwise it is 0.

The developed reactor model has been implemented and solved in MATLAB. In the analysis of a given reaction mechanism the value regions of the reaction rate constants are equally divided. The simulations are performed at randomly selected reaction rate constant combinations from these regions. The analysis gives some mechanisms which fingerprints in different regions of kinetic parameters are the same as the unknown mechanism. This information about the region of kinetic parameters can be applied in the parameter identification process as constraints for the searching variables (i.e. reaction rate constants). If all the mechanisms are analyzed from the list a database is obtained from based on the similarity of the fingerprints the most suitable mechanism can be chosen.

3. Results and discussion

In this chapter the steps of an earlier introduced algorithm are presented in a simple case. The simple reaction system is the hydrogenation of acetylene which produces ethylene at the first step and ethane after a second additional reaction. In this case we do not have an opportunity to perform physical experiments so the “measured” data is obtained from simulation. As it can be seen in Figure 3 the reaction rate constants are from the real ones. Based on the qualitative analysis of the “measured” data it can be seen the amount of component C (acetylene) and D (hydrogen) is decreased all the time during the experiment and the resulted sequences for these two components contain only one episode which is ‘A’. Component A (ethane) is continuously increasing while component B (ethylene) is increasing in the first 2 hours, after that point it is decreasing. That profile can be compressed to the following sequence of the applied primitive episodes: ‘ABC’.

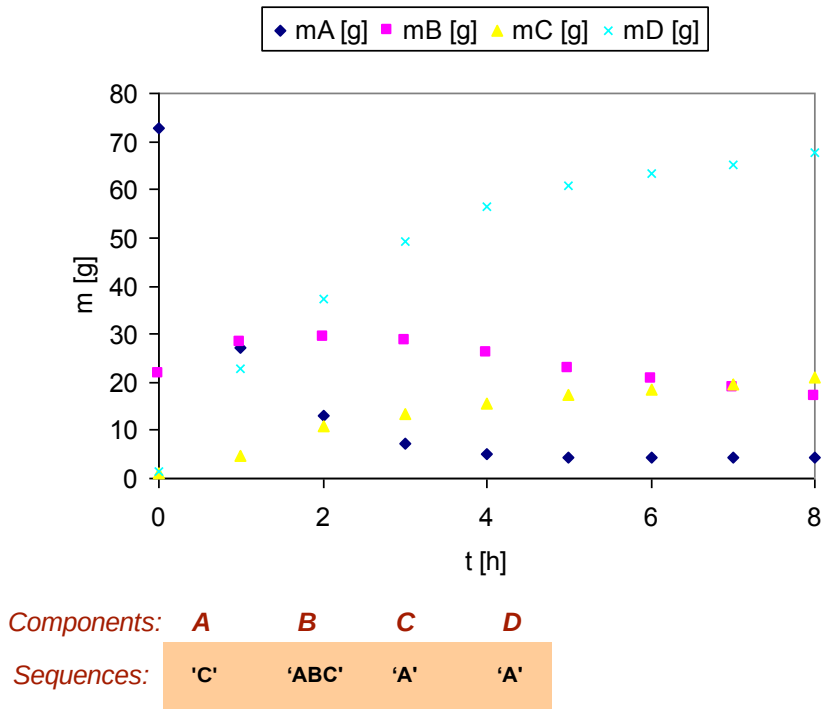

Figure 3: The measured data and the unknown fingerprint

We have sequences for all the components which appear in the investigated reaction system. Hence, after we have completing the component list the possible basic reaction steps can be generated (see Table 1).

Table 1: The possible basic reaction steps

	A (30 g/mol)	B (28 g/mol)	C (26 g/mol)	D (2 g/mol)
r01	1. -1	2. 1	3. 0	4. 1
r02	5. 0	6. -1	7. 1	8. 1
r03	9. 1	10. -1	11. 0	12. -1
r04	13. 0	14. 1	15. -1	16. -1

As we have only four components in our case only four basic reaction steps can be differentiated. As it can be seen in Table 1 the formation and the decomposition of each equilibrium reactions are not erased from the list because of the simple reactor model Eq(1)-(3). Based on the list of basic reaction steps all the possible reaction mechanisms are generated. In this case we maximized the number of reaction steps in each mechanism in three.
In Figure 4 the evaluation of two of the possible reaction mechanisms can be seen. At the top of Figure 4 are the two mechanisms with stoichiometric matrix representation. In the middle of Figure 4 the identified fingerprints for these two mechanisms can be seen. At the bottom of this figure the regions for the reaction rate constants can be seen with the same colour as the resulted fingerprints are written.

The investigated reaction mechanism:

$$\begin{pmatrix} -1 & 1 & 0 & 1 \\ -1 & 0 & 1 & 2 \\ 1 & -2 & 1 & 0 \end{pmatrix} \qquad \begin{pmatrix} -1 & 1 & 0 & 1 \\ -1 & 0 & 1 & 2 \\ -1 & 2 & -1 & 0 \end{pmatrix}$$

The possible fingerprints of the analyzed reaction mechanism:

'BC'	'C'	'A'	'A'	'C'	'DA'	'A'	'A'
'C'	'C'	'A'	'A'	'BC'	'DA'	'A'	'A'
'C'	'BC'	'A'	'A'	'C'	'A'	'A'	'A'

The kinetic constant regions for each fingerprints:

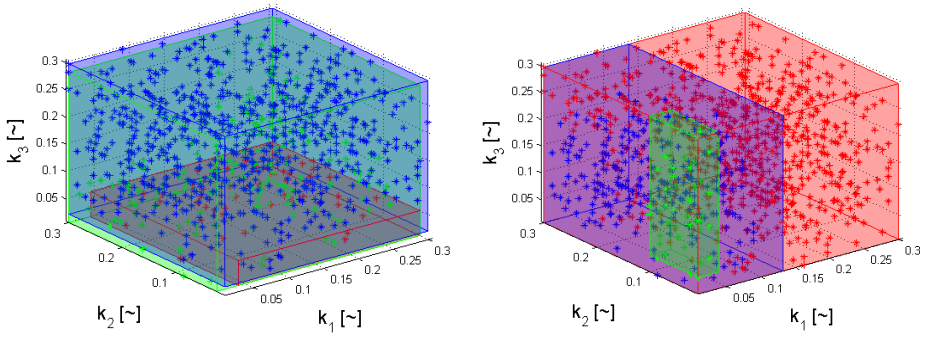

Figure 4: Comparison of two possible reaction mechanisms

4. Conclusions

The reaction mechanism of a reaction system represents all the elementary reaction steps which are required to convert the reagents into products. Hence, the aim of reaction mechanism identification is the determination of the intermediate steps which are leading to the final product. The proposed tool can support this process in case experience is lacking in the identification of reaction mechanism and parameters of kinetic expressions.
The applied structure identification method is based on qualitative trend analysis because using this technique the trends in measured and in calculated profiles can be easily compared. Based on the proposed algorithm for reaction mechanism identification process shown in Figure 5 a tool has been developed in MATLAB (Varga, 2012). In the near future the developed tool can be improved with other reactor models which make possible to apply the tool to process the measured data from different kind of reactors. The developed tool can be downloaded from the following website:

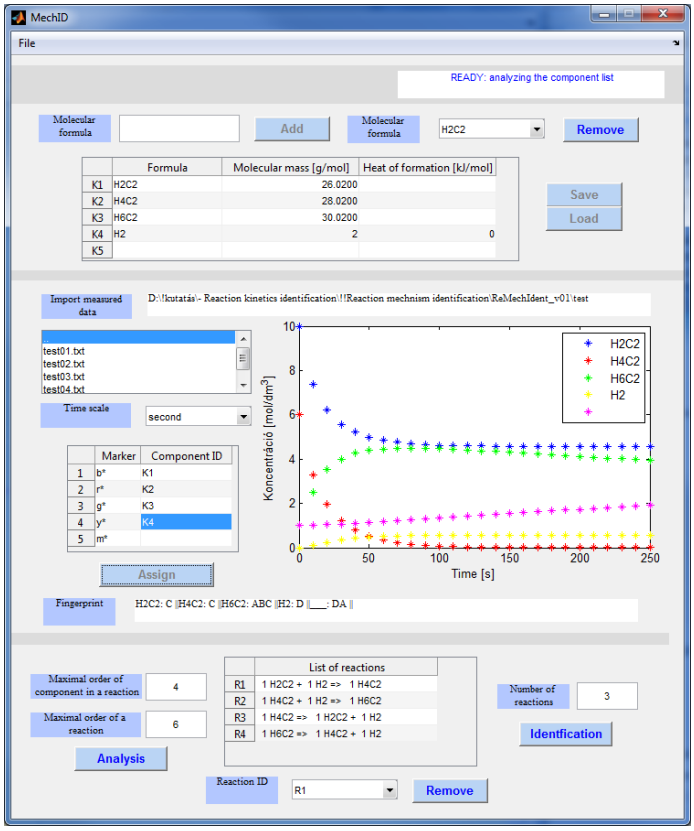

Figure 5: The developed tool to support the reaction mechanism identification process

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