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Parameter Estimation of Complex Chemical Kinetics with Covariance Matrix Adaptation Evolution Strategy

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Abstract

This paper presents a method for parameter estimation of complex chemical kinetics by an evolution strategy which uses a scheme called covariance matrix adaptation. The advantage of this scheme is that a completely derandomized self-adaptation of mutation distribution can be achieved. The used algorithm utilizes even cumulation to improve the performance.

The method was tested on experimental data of ethene pyrolysis and the parameters of two kinetic models depicting the phenomenon were estimated. The models comprised of 37 and 687 reversible reactions respectively. The method successfully estimated the kinetic parameters for both models.

1 Introduction

Evolution algorithms are effective and robust methods for optimization. Their biggest disadvantage is the poor convergence performance and therefore they are most efficient in global optimization problems that have many local optima. They have been used in parameter estimation of complex chemical kinetics, but have not gained popularity over conventional gradient/derivative based methods, which are computationally lighter in simpler parameter estimation tasks. In large parameter estimation tasks, however, evolution algorithms have a clear advantage as the choice of initial parameter values is by far simpler task as it is for gradient/derivative based methods.

Evolution algorithms can be divided in different techniques based on the implementation details. These techniques include genetic algorithm, genetic programming, evolution programming, neuroevolution and evolution strategy. For this paper, an evolution strategy (ES) was chosen for parameter estimation. The selection process in evolution strategies is based on the fitness rankings rather than the actual fitness values and it is deterministic. This is one of the main reasons for the robustness of ESs. Besides selection, mutation is used as a search operator. The step-size of mutation is often governed by self-adaptation to keep the progress in the evolution window. Another technique to ensure the convergence to the optimum of a function is cumulative step size adaptation.

Evolution strategies have been previously used in parameter estimation of complex chemical kinetics by Polifke et al [1]. In that work, a simple $(\mu + \lambda)$-ES by Rechenberg et al. [2] was used. Some improvements to this work has been proposed by Elliott el al [3] including addition of recombination operation, which is occasionally used in evolution strategies to prevent the algorithm to stuck on local optima. Other types of evolution algorithms, mainly genetic algorithms, and also other types of stochastic algorithms, such as particle swarm and differential evolution (DE) have also been applied to parameter estimation in chemical kinetics.

To our work, an evolution strategy with covariance matrix adaptation (CMA-ES) by Hansen and Ostermeier [4] was chosen. Hansen and Ostermeier depict the step to CMA-ES from an ES with isotropic mutation distribution as comparable to a step from a simple gradient-based method to a quasi-Newton method, e.g. a step from local gradient to approximation of inverse Hessian matrix. CMA-ES has already been applied to many real-world search problems. The advantage of CMA-ES over the conventional ESs is the added invariance properties.

The detailed models of tar formation from light hydrocarbons are very complex, consisting of several hundreds of reactions. As the amount of estimated parameters can be as high as three times the amount of reactions, parameter estimation of chemical kinetics for tar formation is a practical example of an optimization problem, for which conventional gradient/derivative based algorithms are difficult to implement. It has been proposed that the limit above which stochastic optimization methods outperform the gradient based methods is as low as ten dimensions.

2 Parameter estimation problem and software

2.1 Parameter estimation problem

The chemical system which the algorithm was tested on is the early stage of tar formation, where heavier gaseous hydrocarbons are formed from light hydrocarbons at elevated temperatures. Two models, which depict the phenomenon, were subject to parameter estimation. One was a detailed kinetic model from Lawrence Livermore National Laboratories (LLNL) [5] and the other one was a reduced kinetic model of our own [6]. The phenomenon is complex and even the reduced model comprises of 37 reversible reactions and 30 species. Both models do give as such a decent fit to experimental data, but to obtain a good fit to experimental data, parameter estimation offered an effective method.

The utilization of conventional parameter estimation algorithms, which are based on derivatives and gradients, would be tedious to implement to a differential equation system of this magnitude because the topology of the surface is detailed. An additional challenge is that parameter estimation for this kind of system is a non-trivial to solve as the rate constants are typically of different magnitude, some of the numerical values are close to the machine precision limit, while others are very large and due to the intrinsic feature of chain-reaction kinetics, for which the rates change rapidly due to branching reactions. These dilemma need to be solved.

2.2 Evolution strategy with covariance matrix adaptation (CMA-ES)

CMA-ES is an evolution strategy which implements two important self-adaptation methods, namely derandomization and cumulation. With cumulation, the information from the past generations is used in the self-adaptation by considering the search-path the population has undergone. Derandomization is a process, in which the mutation distribution is changed deterministically so that the probability of the previously successful steps is increased.

The CMA-ES has been tested on multi-modal test functions by Hansen and Kern [7]. In their work, the performance of the CMA-ES algorithm is compared to the performance of the differential evolution algorithm, the Robust Evolution Strategy (RES) and Local Optima Smoothing (LOS) restart BFGS algorithm. Only on additively separable functions, the CMA-ES was outperformed by the DE algorithm. Therefore, CMA-ES is seemingly a plausible candidate for an effective parameter estimation algorithm for complex chemical kinetics.

According to Hansen and Ostermeier [4], roughly $10n$ function evaluations are needed for a significant change in mutation distribution shape and strategy behaviour cannot realistically be expected to improve until $30n$ function evaluations have been run. A complete adaptation can take even $100n^2$ function evaluations and between 100 and $200(n+3)^2$ function evaluations are recommended to get maximal advantage from the self-adaptation.

2.3 Parameter estimation software

As the parameter estimation software, which we have been previously been using, failed to perform parameter estimation on the system described in section 2.1, we were forced to create in-house parameter estimation software. This software was required to be able to perform the parameter estimation on complex chemical kinetics. There are program codes, which can simulate gas-phase radical chemistry. It is obvious that if such software could be modified to do the parameter estimation, a lot of time could be saved. CHEMKIN II [8] has been designed primarily to simulate gas-phase radical chemistry and the numerical issues intrinsic to this kind of system have been successfully solved already. As CHEMKIN II was distributed with the source code, it offers a flexible alternative for implementing some in-house code. In our case, a post-processor and a driver program were needed. Therefore, it was chosen to be used in our parameter estimation software.

Other choice to be made was the optimization algorithm. According to literature findings, stochastic algorithms have been effective in parameter estimation of such problems. Due to the reasons presented in section 2.2, a CMA-ES algorithm by Hansen and Ostermeier [4] was selected.

The used software consists of SENKIN [9] module of CHEMKIN II software package, CMA-ES algorithm from Hansen and Ostermeier and a post-processor of our own. The software is schematically illustrated in Figure 1.

The initial strategy parameters are manually inserted to CMA-ES algorithm. Likewise, the model is written to an input file to the SENKIN module of the CHEMKIN II software package. The parameter estimation is started and CMA-ES sends the proposed coefficients for parameters to in-house driver program. The SENKIN module simulates the model with parameter values, which are calculated to be the product of the proposed coefficient and literature value of the respective kinetic parameter. After a successful simulation, the in-house driver starts the in-house post-processor, which calculates the sum of squares of the simulated

values and our experimental results. The post-processor returns this value to driver which returns it to CMA-ES algorithm as a fitness value. At the same time, both in-house modules record the all-time best values. CMA-ES then proposes new values for coefficients, which undergo the same process until a termination condition is met. When a termination condition is met, CMA-ES produces the results of its workings. The in-house driver produces a CHEMKIN input file with best found parameter values and post-processor gives results in a form, which can easily be plotted graphically.

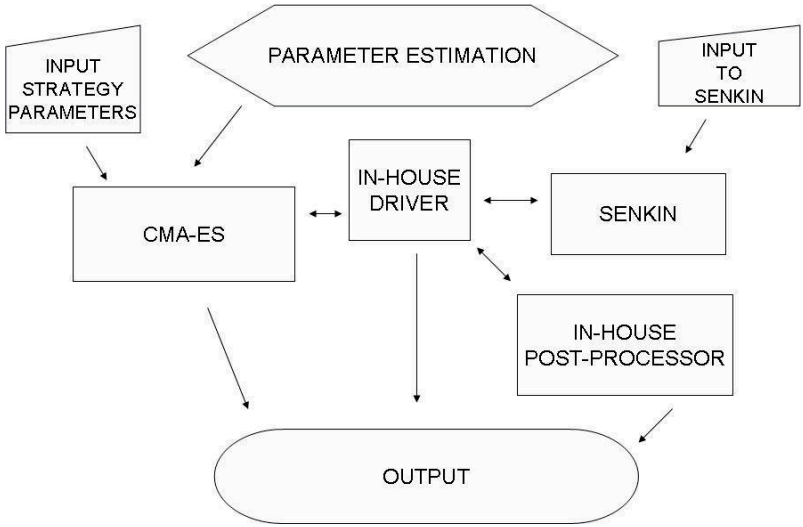


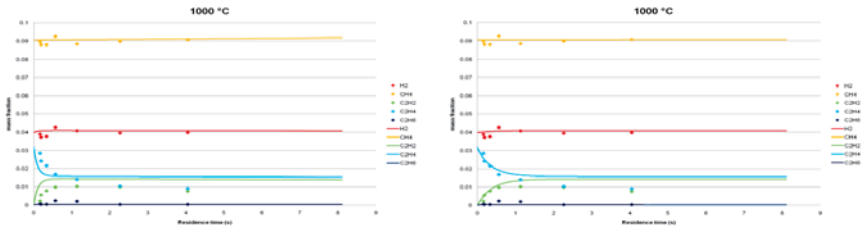
Figure 1: A schematic view of the parameter estimation software

3 Results and discussion

The goodness of the fit was estimated by the sum of squares, which was calculated from experimental results of our own. Kinetic experiments were conducted at six temperatures from 500 °C to 1000 °C and for two different compositions. Both mixtures contained 2 mol-% ethene and 10 mol-% methane and the other one had 35 mol-% of hydrogen**.** Nitrogen was used as a balance gas. All in all, 120 experimental points were recorded for the calculation of sum of squares. The experimental setup is presented in detail in another article [10]. In case of

a detailed kinetic model from LLNL, the sum of squares was lower, even though the magnitude was the same as with our reduced kinetic model prior to the parameter estimation.

A regression analysis of the model predictions and the experimental values was performed by the data analysis toolpack in Excel. It was observed that the R^2-value**,** the coefficient of determination, increased significantly by the parameter estimation and was 0.966 after the parameter estimation. The R^2-value is a measure of how likely the model predicts the future outcomes. The sum of square values in both cases were over 10 % lower after the parameter estimation compared to prior the parameter estimation. Graphical illustrations of the experimental values compared to model predictions prior to and after parameter estimation are presented in Figure 2a-b.



(b) Model predictions after parameter estimation

Figure 2: Graphical illustration of the model predictions (a) prior to parameter

In case of the LLNL model, the advantage of the adaptation of the mutation distribution could not be observed as the parameter values were not allowed to change more than 5 % and the best combination of parameter values was found at less than $30n$ function evaluations which is according to Hansen and Ostermeier the limit for the adaptation to improve the strategy behaviour. In the case of our reduced model, more evaluations were required to obtain a solution with an acceptable accuracy. Therefore, the adaptation did have time to evolve. The same restriction of 5 % was applied even here. Even in this case, the full advantage of the adaptation as the limit of $100n^2$ function evaluations was not reached.

During the development of our model, we tried to perform the parameter estimation on preliminary models, too. In a case when the estimated parameters were not close to the literature findings, considerably more function evaluations were needed to reach a satisfactory

accuracy for the model. In attempts like these, no restrictions were applied. This indicates that CMA-ES could be an interesting candidate for parameter estimation in such applications, where the magnitudes of the parameters are unknown and the amount of parameters is large. Possible applications are problems, in which diffusion and/or adsorption effects are added to complex chemical kinetics.

Hansen and Kern [7] have reported that increasing the population, in many cases, considerably increases the performance of the algorithm. In our applications, this kind of behaviour could not be observed in significant magnitude. As some test functions in their report did not either exhibit such behaviour, this cannot considered a surprising result. It is though possible that the population size should have been increased even more than we did to obtain an increase in algorithm performance.

Different parameter estimation approaches were tested. We tried to estimate all the parameters in the modified Arrhenius equation presented in Eq. 1 and different combinations of them. The most efficient way was to estimate only one parameter. Intuitively, this is clear as the size of covariance matrix increases but the amount of data from which it is estimated does not increase.

$$k = A * \left(\frac{T}{T_0} \right)^n * e^{\frac{-E_a}{R*T}} \tag{1}$$

4 Conclusions

The software successfully estimated the parameters of the complex chemical kinetics. The modeled phenomenon was depicted by two models, a semi-large model of 37 reversible reactions and a large model comprising 687 reversible reactions. In both cases the sum of squares was significantly lower after the parameter estimation than it was prior to the parameter estimation.

The adaptation of covariance matrix could not shown to have an importance in case of a detailed kinetic model, in which the parameter values were allowed to change only a little, while the values of parameters were close to literature values. On the other hand, when the magnitude of the parameter values was unknown, CMA-ES did offer an efficient alternative for the parameter estimation.

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