Generalized Incremental Model Identification for Chemical Reaction Systems

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Identification of kinetic models and estimation of kinetic parameters in chemical reaction systems can be done using *Incremental Model Identification* (IMI). By using IMI, it is possible to separate the effect of the different reactions and thus investigate each reaction individually. In contrast, with simultaneous approaches, it is necessary to work with a complete model that includes a rate candidate for each reaction, which might lead to a large number of possible model combinations. Hence, IMI allows faster computation of the identified models and estimated parameters [1]. There exist essentially two main approaches for IMI: extent-based IMI and rate-based IMI. In extent-based IMI, reaction rates are integrated to yield extents, and the parameters are estimated via least squares by fitting these simulated extents to experimental extents obtained from measured concentrations [2]; in rate-based IMI, the parameters are estimated via least squares by fitting simulated rates to experimental rates obtained by differentiation of measured concentrations [3].

This contribution proposes a generalized IMI method that offers much more flexibility in the use of measurements, particularly in the way the various measurements are weighted. The parameters are estimated via weighted least squares by comparing simulated and experimental extents. The peculiarity consists in comparing extent values not only at the measurement points but for all possible time intervals between measurement points. Then, it can be shown that both the extent-based and rate-based IMI can be reformulated as particular cases of this generalized method. For example, the extent-based method would correspond to positive and equal weights for all time intervals that start at time zero, while the rate-based method would correspond to positive and equal weights for all time intervals with a length of one sampling period. This reformulation allows the investigation of new approaches by testing compromises between different methods, which can potentially result in a better IMI method.

With such a generalized method, it is also possible to test if there is an optimal weight distribution or, more generally, if there are important features in the weights to best perform model identification. The effect of the weight distribution on (i) the accuracy and precision of the parameters, and (ii) the model discrimination power can be investigated via different optimization methods, such as classic gradient-based algorithms or genetic algorithms. The different directions followed to find the best weight distribution are illustrated with simulated examples, and these results are compared to extent-based and rate-based IMI.

[1] Bhatt et al., Chem. Eng. Sci., **2012**, 83, 24-38
[2] Bhatt et al., Ind. Eng. Chem. Res., **2011**, 50, 12960-12974
[3] Brendel et al., Chem. Eng. Sci., **2006**, 61, 5404-5420