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# Hierarchical Multiscale Model-based Design of Experiments, Catalysts, and Reactors for Fuel Processing

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## Abstract

In this paper a hierarchical multiscale simulation framework is outlined and experimental data injection into this framework is discussed. Specifically, we discuss multiscale model-based design of experiments to optimize the chemical information content of a detailed reaction mechanism in order to improve the fidelity and accuracy of reaction models. Extension of this framework to product (catalyst) design is briefly touched upon. Furthermore, we illustrate the use of such detailed and reduced kinetic models in reactor optimization as an example toward more conventional process design. The ammonia decomposition on Ruthenium to produce hydrogen and the water-gas shift reactions on Platinum for converting syngas to hydrogen serve as illustrative fuel processing examples of various topics. Finally, opportunities for process design and control in portable microchemical devices (lab-on-a chip) are discussed.

**Keywords**: Multiscale, Process and Product Engineering, Model-Based Design of Experiments, Reactor Optimization, Microreactors.

## 1. Introduction

There is an ever increasing number of portable electronic devices, such as cellular phones, laptops, personal data assistants, personal transportation, night vision goggles, GPS, unmanned aerial vehicles, etc. that necessitate portable power generation. Traditional battery technology often results in power supply systems that either are too heavy, do not last long enough, or both. For military applications, the power requirements for special missions can often exceed the capacity of the dismounted soldier's batteries [1]. Single-use batteries are often disposed of, resulting in heavy metals and other toxic substances being released. Hence, hydrocarbon-fuelled systems are envisioned to be replacements of current battery technology for civilian and military applications [2,3].

Table 1 shows different power sources and their mass-based energy densities. In general hydrocarbons possess two orders of magnitude higher energy densities than lithium ion batteries. Conversion of chemical energy of hydrocarbons into electricity

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can then result in lighter or longer lasting portable devices. If greater than 1% of chemical energy could be converted into electricity, an improvement over batteries could be achieved. Additionally, hydrocarbons, if used properly, only release water and carbon dioxide. Often times it takes hours to recharge batteries, whereas hydrocarbon-based devices can be refueled quickly by simply adding more fuel. Successful commercialization of portable power systems depends on the development of robust fuel processing schemes that enable safe, efficient, economic, and convenient operation.

Table 1: Energy densities of different sources. The energy density of combustion-based sources is based on complete combustion to carbon dioxide and liquid water at 25 ºC and 1 atm.

| Source | Energy Density [MJ/kg] |
|---|---|
| Lead acid Batteries | 0.0792 |
| Nickel cadmium batteries | 0.158 |
| Lithium ion batteries | 0.468 |
| Methanol combustion | 22.7 |
| Heating oil combustion | 42.5 |
| Gasoline combustion | 45.8 |
| Propane combustion | 50.3 |
| Methane combustion | 55.5 |
| Hydrogen combustion | 142 |

In this paper, we first present an overview on multiscale simulation focusing on the idea of hierarchical multiscale modeling of chemical reactors that has recently been proposed for model development and/or parameter estimation [4,5]. Then we present examples of using these models for model-based design of experiments with the objectives of (1) maximizing the information content of a reaction model, (2) reduction of model complexity, (3) carry out catalyst design, and (4) optimal reactor design. These are some of the first demonstrations toward the direction of multiscale model-based product and process engineering in the area of fuel processing for $H_2$ production, which could, in conjunction with fuel cells, be used for portable power generation. Alternative routes of harvesting energy from fuels, such as thermoelectrics [6], thermo-photovoltaics [7], or micro-engines [8,9] are not discussed here.

## 2. Multiscale Modeling: Process vs. Product Engineering

Multiscale modeling is the enabling science that seamlessly and dynamically links models and phenomena across multiple length and time scales, spanning from quantum scales to macroscopic scales, in a two-way information traffic manner (see Fig. 1) [10-14]. Macroscopic scales may include a process or an entire plant. The typical objective of multiscale modeling is to predict macroscopic behavior, such as selectivity, conversion, pollutant levels, hot spots, etc. from first principles. Multiscale modeling involves computing information at smaller scales and moving towards the top of the "simulation ladder" by coarsening degrees of freedom as one goes from finer to coarser scales. Prediction of large-scale process performance based on small-scale information is termed bottom-up approach or upscaling. Since it can be easily assimilated with process alternatives, it is congruent with the traditional objective of *process engineering*. Recent reviews on multiscale modeling of chemical reactors, systems biology, and materials highlighting this view are given in [14-16] and references therein.

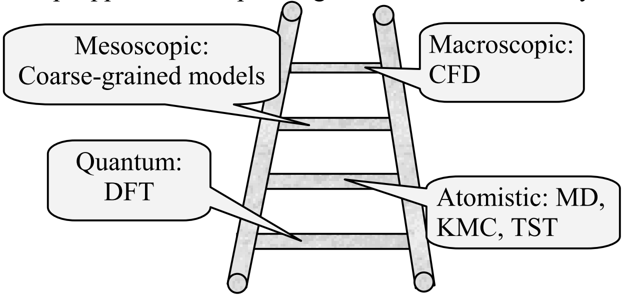

Figure 1: Schematic of multiscale simulation ladder with main scales and typical tools. Information flows up (bottom-up) and down (top-down) the ladder. The step narrowing indicates the loss or coarse graining of information as one moves from lower to upper scales. For more discussion, see [14]. DFT=Density function theory; CFD=Computational fluid dynamics; MD=Molecular dynamics; KMC=Kinetic Monte Carlo; TST=Transition state theory.

A probably more important but relatively unexplored role of multiscale modeling is in *product engineering*. Coupling of models between scales provides a ‘descriptor’ or a ‘ladder’ linking atomistic scale information of materials with macroscopic scale processing. Such a descriptor provides a unique opportunity for product engineering. In the context of multiscale simulation, product engineering can be viewed as the possibility to define desirable performance (objective functions) at the macroscopic scale and then come up with better materials of suitable atomistic structure and possible synthesis protocols via the use of multiscale modeling. Examples can entail the identification of better (cheaper, more stable, more active and selective, etc.) catalysts, of optimal pore size distribution, of templates that produce a desirable zeolite, etc.

Combined process-product engineering is obviously also very important. In particular one is often interested in manipulating variables at the macroscopic scale, e.g., change flow rates and composition, but achieve control at the nanoscopic length scale either by optimum design or model-based on-line control [17-19]. An example is the ability to control the particle size distribution, the particle shape, and the atomistic packing of materials in crystallization of proteins. Atomistic details of intermolecular forces and templating effects along with more traditional variables, such as local pH and supersaturation, significantly impact polymorphism and thus whether one gets the right material. Yet, macroscopically manipulated variables control the local (i.e., at the nanoparticle scale) supersaturation, concentration of templates, and pH, and therefore the local gradient in chemical potential that in turn affects growth rate and packing.

Multiscale model-based control is currently plagued by the tremendous computational cost of multiscale simulation and the difficulty of having numerous nanoscopic sensors and actuators distributed in a system. The former can be handled using suitable reduced models. Model reduction of complex multiscale models is an important research direction [14] that will only be discussed briefly later in this paper. The prospect of using a small number of *mobile sensors and actuators* that can collect information from ‘optimal’ spatial and temporal locations is a promising avenue to overcome the latter and enable product-process system engineering.

### *2.1. Hierarchical Multiscale Simulation: Building on Ideas from Conceptual Process Design for Model Development*

The above multiscale science vision, while stimulating, is currently too ambitious to be of practical value for the design and control of complex systems, such as those encountered in microchemical systems for portable fuel processors. There are numerous reasons rationalizing this fact. Consider the example of quantum mechanics at the smallest scale. Density functional theory (DFT) is breaking new grounds in the parameter estimation front. Recent work sets a paradigm for DFT-based parameter estimation on single crystals [20-26]. While DFT is the only truly founded theoretical technique of practical interest for catalysis that has great potential, it is practically limited to small molecules, to single crystals, and to specific coverages and is semi-quantitative (at best) in nature. First, even most of the best DFT calculations have an accuracy of ± 5 kcal/mol in predicting activation energies. As a result, reaction rates are not as accurate and this uncertainty is important in predicting activity and selectivity especially at low temperatures. Second, DFT simulations are carried out on idealized single crystals that are of interest in surface science studies but can be irrelevant for practical catalysts that are polycrystalline or defected nanoparticles spread on a support. Third, DFT calculations are carried out at certain coverages. The multicomponent nature of complex fuel processing reactions and the drastic variation of dominant coverages of surface species with varying operating conditions make parameterization of surface kinetics (as a function of coverages) a combinatorial problem of large dimension that is currently beyond the reach of computational capabilities. Forth, the number of reactions needed to describe the chemistry of complex reactions is large. For example for the water-gas shift (WGS) reaction discussed below, 46 elementary-like reactions may be considered [4,27], whereas for the partial oxidation of methane more than 100 reactions are employed [28]. These large reaction networks hint to the inability of expensive DFT calculations to deliver these many parameters. Fifth, it has been recognized that the active sites in many reactions involve steps, kinks, and other defects whose size and/or density is such that it is impossible to even fit them in the unit cell of a DFT calculation. Sixth, DFT is inaccurate for weak, e.g., van der Waals, interactions and cannot treat well small activation barriers. Some of these limitations are known as materials gap (inability of DFT to deal with multiple scales shown in Fig. 1); the rest are associated with the CPU intensive nature of DFT.

At the mesoscopic scale, kinetic Monte Carlo (KMC) simulation with large kinetic mechanisms is still in embryonic stages [21,29]. KMC is seriously plagued by fast diffusion and more generally stiffness and the inability of reaching large length scales [30]. Coarse-grained KMC is a new tool that could overcome these problems [31].

At the reactor scale, computational fluid dynamics (CFD) simulations are employed when the continuum approximation is valid. Yet, CFD simulations are very intensive especially when flows are turbulent, when reaction networks are large, and when geometries are complicated. Process engineers use computationally efficient software, such as ASPEN and HYSYS, to carry out optimization and process control studies. This task is obviously impossible to achieve using CFD.

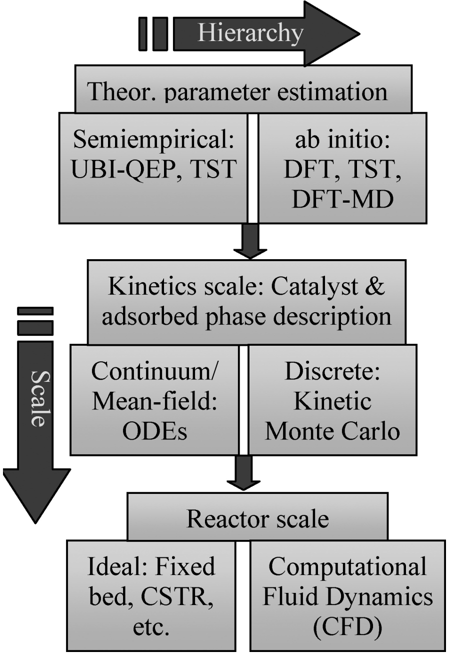

Figure 2. Hierarchy of chemical kinetic and reactor models at various scales. UBI-QEP: Unity Bond Index Quadratic Exponential Potential. See Fig. 1 for other abbreviations.

Instead of trying to simulate all phenomena at all scales with the highest accuracy, one realizes that only certain reactions, species, phenomena, and some of the scales are in reality crucial for accurate prediction of macroscopic properties. The idea of *hierarchical multiscale modeling* and simulation is then to start with the simplest possible “sound” model at each scale and identify the important scales and (‘active’) model parameters at each scale. Once this is accomplished, one assesses the model accuracy by comparison with data and potentially improves the model of the important scale(s) and the associated active parameters using a higher-level model or theory. For example, the simplest identification tool employed extensively and successfully in chemical kinetics is local sensitivity analysis [32]. Upon improvement of models and parameters, another iteration is taken until convergence is achieved, i.e., the important scales and parameters do not change between successive iterations. This approach is reminiscent of conceptual process design used for chemical flow sheets, where detailed design is done only after several iterations of calculations of increasing complexity are done [33]. Specific tools employed in hierarchical multiscale chemical reactor model development are depicted in Fig. 2. The model predictions at each scale become more accurate as one goes from the left to the right of the figure, at the expense of increasing computational intensity.

### *2.2. Data Injection into Multiscale Models for Parameter Refinement or Scale-Model Replacement*

Irrespective of the power of multiscale modeling, model parameters, such as diffusivities and activation energies, and measured quantities, such as catalyst surface area, have always an *uncertainty*. As a result, models are almost never in perfect agreement with experimental data. In other instances the computational requirements are so large that one may have to completely bypass the modeling of a scale, typically of the quantum one. It is therefore desirable to estimate or refine the active parameters or fill in a missing model of a particular scale using experimental data instead of higher-level theory/model discussed above. This injection of data into a multiscale model is needed to increase its predictive capabilities and can be done using data at one or more scales of the ladder (see Fig. 1).

Parameter estimation or refinement and model replacement become then an integral part of multiscale model development. A complication is that multiscale models are typically complex and computationally intensive and involve discrete, often stochastic, models at some scales. Therefore parameter estimation can be very time consuming and with noisy models in comparison to traditional parameter estimation of deterministic models. Response surface methods (RSM) could be invaluable in achieving this objective at minimal computational cost [34]. Development of more accurate and efficient RSMs should be an important objective of the systems community.

Hierarchical multiscale modeling can be extremely valuable also when parameters are completely unknown. For example, one uses a mean-field, continuum model (such a model assumes spatial homogeneity at the microscopic scale) to estimate parameters and then uses these parameters as a good initial guess in a KMC model (this model can naturally account for microscopic heterogeneity, surface diffusion, defects, etc.) [5,35]. As another example, one uses a deterministic continuum model to estimate parameters and these parameters are then refined using the corresponding stochastic simulation that considers fluctuations and correlations in species populations.

The hierarchical multiscale modeling should be exercised with caution. Its success relies in the various models of a scale being ‘structurally’ the same. For example, a linear lower level model may not capture the behavior, such as bifurcations, of a nonlinear higher-level model. In these instances one may hope to be successful only locally or needs to develop better lower level models.

### *2.3. An example of $NH_3$ decomposition on Ru for $H_2$ production*

The specific hierarchical multiscale framework for chemical reactors is depicted in Fig. 2. At the lowest theoretical level (left column), detailed microkinetic models are developed for the surface chemistry consisting of elementary-like reaction steps. Pre-exponentials are set based on Transition State Theory (TST) and activation energies are computed using the semi-empirical Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) theory [36], using heats of chemisorption as inputs. These inputs can be obtained from experiments (preferred), DFT, or estimated using the UBI-QEP method. The output of the UBI-QEP method is activation energies of all surface reactions as a function of surface coverages.

Reaction rates are determined using the mean-field approximation and are passed into a suitable, simple reactor scale model that accounts for transport via standard mass and heat transfer correlations. The entire framework is an automatic ‘wrapper’ of Surface

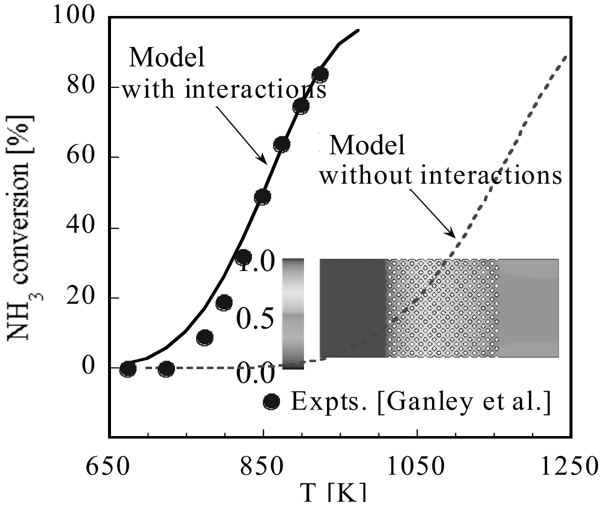

Figure 3. Comparison of predictions for $NH_3$ decomposition on Ru with (solid line) and without (dashed line) adsorbate-adsorbate interactions in a CFD simulation, shown as inset [39], against data (symbols) of [40].

Chemkin [37] and allows users to simulate pseudo-homogeneous reactors, such as a fixed bed reactor, and compare different catalysts. At this stage one can inject data to refine parameters or use more advanced theoretical tools, such as DFT, KMC, or CFD depicted in the right column of Fig. 2, to improve the model and parameters at the scale(s) that appears most critical. In our work we have used data injection to refine pre-exponentials only and DFT to refine energetics. The latter has mainly been used to account for surface coverage effects that are nearly impossible to obtain experimentally but can be crucial in affecting reactivity and selectivity [38]. Instead of solving the combinatorial problem of computing all interactions between all species in a brute-force manner, we identify the most abundant surface species (typically 1 or 2) by running simulations and carry out only a small number of DFT calculations for those relevant interactions.

Advantages of this theoretical framework include: (a) its high speed (sub-seconds), (b) reasonable predictive capabilities in most cases, (c) easy exploration of alternative reaction paths (this is important to ensure that most relevant chemistry is included), and (d) creation of insights into the important chemistry. An example of performance of a detailed kinetic model of $NH_3$ decomposition on Ru, consisting of 6 reversible reactions, against data from a post microreactor is shown in Fig. 3.

## 3. Model Reduction

The models obtained using the hierarchical multiscale framework are often very complex and computationally demanding. The aim of these models is the accurate prediction of macroscale properties, such as conversion. Ideal reactors (lower hierarchy at the reactor scale in Fig. 2) seldom represent the actual system accurately, and hence, more realistic CFD models need to be used. Using complex kinetic models (higher hierarchy at the kinetics scale) with complex CFD models (higher hierarchy at the reactor scale) represent a large computational burden. As a result, model reduction is required to obtain computationally tractable, physically meaningful models.

Mathematical tools such as principal component analysis (PCA), approximate inertial manifold (AIM), etc. have been used for model reduction at various scales (for example, see [39]). Additionally, scaling analysis has been used to simplify the complexity of reactor models, whereas identification of the rate determining step (RDS) or the use of small scale asymptotics is useful at the kinetics scale [40]. For example, [41] simplified a transient CFD model using scaling laws, and solved a pseudo-steady 1D model in the gas phase and a transient 3-D model in the solid phase. [42] used boundary layer approximation and scaling analysis to reduce a 2D elliptic model into a more computationally tractable parabolic model, whereas, [43] reduced the kinetic model consisting of 6 reversible reactions (discussed in the previous section) for ammonia decomposition and used the resulting 1-step chemistry in CFD reactor modeling for design of integrated microdevices for hydrogen production [44]. These are just some examples of model reduction but model reduction is unquestionably an essential step in multiscale model development (Fig. 1) and in linking complex models to process and product optimization and control.

## 4. Model-Based Design of Experiments: Maximizing Chemical Information Content

Experiments are typically carried out at certain conditions and it is often found that only a small number of kinetic parameters are active under those conditions. A natural question is whether one could design experiments based on a model, rather than statistical design, in order to increase the number of active model parameters and the accuracy of parameter estimation from data. The benefit of increasing the number of active parameters is that one could either validate or extract additional and possibly more accurate kinetic parameters. A parameter $p_j$ is most active when the response $R_i$ of the model with respect to this parameter is highest, i.e., when the absolute value of a sensitivity coefficient $|\partial \ln R_i / \partial \ln p_j|$ is largest. During the estimation of kinetic parameters, identifiability analysis [45] could determine the extractable ones.

Once optimum operating conditions for maximizing the sensitivity coefficients of the responses with respect to the identifiable parameters in the mechanism have been determined, experiments need to be conducted to test the model. Correct prediction of the best operating conditions depends on how good the initial values of parameters of a model are. Therefore, an iterative approach may be needed. Given that lower level models are used to estimate parameters, model predictions are reasonable even in the first iteration and the search leading to better models and parameters is physically constrained, i.e., convergence is usually attained in 1-2 iterations. Next, we outline the elements of the proposed approach. Then we illustrate the procedure using our microkinetic mechanism for $NH_3$ decomposition on Ru [38] as an example.

### *4.1. Identifiability Analysis*

One performs a sensitivity analysis with respect to the mechanism parameters to obtain a sensitivity matrix g

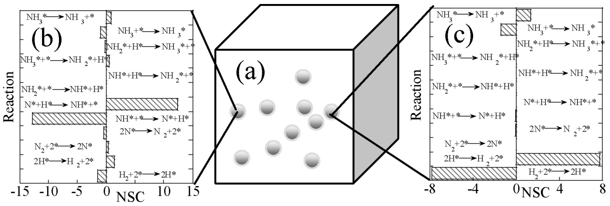

Figure 4. (a) Schematic of global Monte Carlo search in experimental parameter space (represented as a 3D cube for graphical purposes; each (yellow) sphere represents a point randomly picked in space) to identify conditions that sensitize kinetics parameters. (b) and (c) Examples of an actual sensitivity analysis carried out under different conditions. The sensitive (active) parameters can vary considerably in parameter space.

$$g = \left[ \partial R_i / \partial p_j \right], \tag{1}$$

where $R_i$ is the vector of measured model response (e.g., $NH_3$ conversion), p is the vector of parameters (e.g., pre-exponentials), n is the number of model responses, and m is the number of parameters. Then the Fisher Information Matrix (FIM) is calculated

$$FIM = g^T * g\,. \tag{2}$$

If the determinant of FIM is zero, some parameters are interdependent and not identifiable. These parameters have to be removed and the computation of the FIM repeated.

Subsequently, one calculates a correlation coefficient (cc) to judge whether any two identifiable parameters can be estimated within the measurement error in the experiments. cc is given as

$$cc_{i,j} = \frac{FIM^{-1}(i,j)}{\sqrt{FIM^{-1}(i,i) \times FIM^{-1}(j,j)}} \tag{3}$$

and can vary from –1 to +1. Larger absolute values (away from 0) indicate higher correlation between parameters. Every parameter is self-correlated ($cc_{i,i} = 1$). Even though some parameters are identifiable, based on the determinant criterion, they could be highly correlated, so it may be difficult to estimate them separately given measurement error. Such parameters should be removed and the analysis repeated, so that only the identifiable, less correlated parameters are estimated from the experimental data.

### *4.2. Global Stochastic Search*

We perform model-based design of experiments to maximize the number of active parameters and the values of sensitivity coefficients. In particular, a global search in *experimentally feasible* parameter space is conducted on the computer, using a Monte Carlo (MC) global search algorithm (see Fig. 4a). At each point in parameter space, a reactor simulation is run using the current detailed kinetic model along with a local sensitivity analysis of experimentally measured responses with respect to kinetic parameters. Our objective is to identify suitable combinations of experimental variables that sensitize the maximum number of kinetic steps, i.e., identify experimental conditions where the most abundant reactive intermediate (MARI) and the rate determining step (RDS) change, providing additional kinetic information. Herein the FIM is employed, following the methods of [46], to systematically screen and organize the results of the global MC search.

### *4.3. Illustration Using the $NH_3$ Decomposition Reaction on Ru*

The microkinetic model of [38] for $NH_3$ decomposition on Ru has 12 pre-exponentials. Using a continuous stirred tank reactor (CSTR) model, we carry out sensitivity analysis of the $NH_3$ exit mass fraction with respect to the pre-exponentials at 700 randomly selected operating conditions within the ranges shown in Table 2. It is found that the determinant of FIM is non-zero. Therefore, all pre-exponentials are identifiable over the operating ranges. However, calculation of the correlation matrix shows that the backward pre-exponentials are highly correlated with the forward ones (an expected result since the forward and backward ones are related to each other via thermodynamic constraints). Therefore, the backward pre-exponentials are eliminated and the analysis is repeated.

Table 2. Range and scaling type of operating variables used to convert them into the [0,1] interval.

| Operating variable | Min | Max | Scaling |
|---|---|---|---|
| Temperature, T [K] | 500 | 1000 | Linear |
| Pressure, P [atm] | 0.1 | 10 | Log |
| Residence time, $\tau$ [s] | 0.05 | 5 | Log |
| Catalyst area per unit reactor volume, A/V [$cm^{-1}$] | 150 | 15000 | Log |
| Inlet $H_2$ mole fraction | 0.0 | 1.0 | Linear |
| Inlet $NH_3$ mole fraction | 0.0 | 1.0 | Linear |
| Inlet $N_2$ mole fraction | 0.0 | 1.0 | Linear |

With only the forward pre-exponentials, the determinant of FIM is non-zero and the correlations are not very high either; therefore, all six pre-exponentials are identifiable. Fig. 5 shows the correlation coefficients for all reactions based on 700 operating conditions. As expected, each parameter is completely correlated with itself ($cc_{ii}$=1). $H_2$ adsorption and $NH_3$ adsorption ($cc_{16}$ and $cc_{61}$) have ~80% correlation, indicating that independent extraction of pre-exponentials could be difficult and higher experimental accuracy might be required.

The sensitivity coefficients change drastically within the parameter space, as shown in Figs. 4b, 4c, and 6 and so does the RDS (see Fig. 6). This implies that sufficient sampling of parameter space can indeed provide new chemical insights.

Within parameter space, conditions with the largest normalized sensitivity coefficient for each identifiable parameter are found, simply by sorting the global search sensitivity data. To avoid non-interesting conditions of low $NH_3$ conversion and to minimize

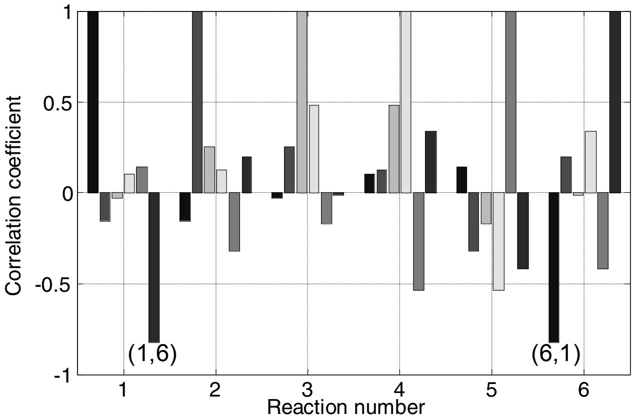

Figure 5. Correlation coefficients for all identifiable pre-exponentials in the microkinetic mechanism for $NH_3$ decomposition on Ru. Some reaction pairs are labeled for ease of visualization.

experimental uncertainties, a threshold of 5% conversion is applied while selecting best operating conditions. Values of optimal operating conditions are depicted in Fig. 6. Subsequently, experiments must be conducted at the identified conditions to test predictions and further refine model parameters (if needed one can take another iteration to refine parameters). At this stage refinement of heats of chemisorption (another model input) and most sensitive pre-exponentials could simultaneously be carried out.

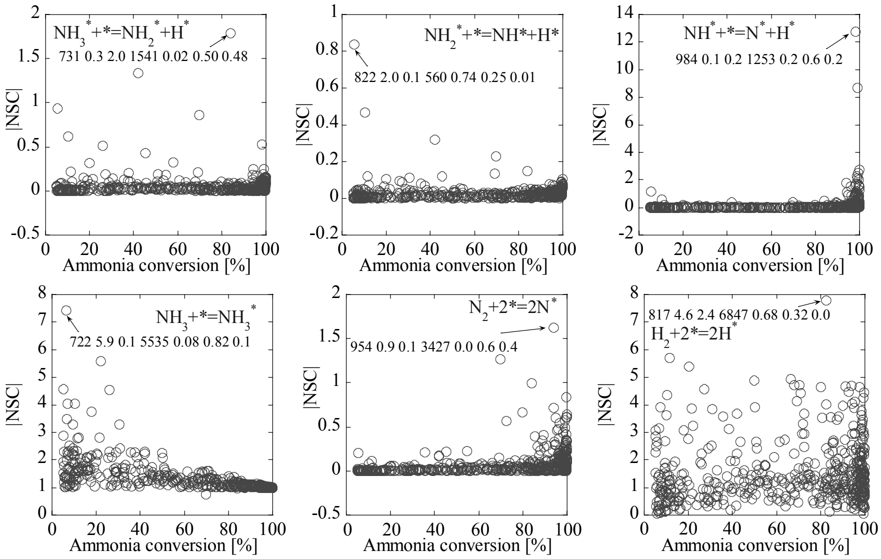

Figure 6. Absolute values of normalized sensitivity coefficients (NSC) from global MC search in parameter space vs. ammonia conversion. The values of optimum parameters of T [K], P [atm], $\tau$ [s], A/V [$cm^{-1}$], and inlet mole fractions of $H_2$, $NH_3$, and $N_2$ are displayed in this order at each maximum NSC.

With the growing success of high-throughput experimentation, the above framework could be applied for faster and more reliable development of microkinetic mechanism parameters that contain valuable chemical information about the adsorbates and the catalysts.

## 5. Toward Model-Based Catalyst Design

By carrying out the above procedure for many catalysts, a library of kinetics models can be developed. We propose that this library can assist in catalyst design. This would then be an example of product design mentioned above. At the simplest level, the catalyst composition becomes a manipulated variable and optimization can lead to better catalysts formulations that can guide high throughput experiments by narrowing down the huge parameter space. This idea awaits experimental validation.

## 6. Use of Microkinetic Models for Reactor Optimization

The design of any chemical system involves tradeoffs, and hence optimizing a process flow sheet is a frequently studied problem [47]. For microreactors, the objective function is cast as maximization of performance, such as yield or selectivity, or as a complex economic function. One of the more conceptually straightforward goals is to use the hierarchical multiscale reactor models to determine the optimal reactor network and operating conditions that optimize the objective function subject to new constraints arising at the microscale (see next section).

The methods for reaction network synthesis can broadly be classified into two main types: attainable region (AR) methods and superstructure optimization methods. [48] defined the AR as a set of all physically realizable reactor outcomes for a given feed, and presented a geometric method to determine the AR in the concentration space. The reactor network that yields the maximum achievable performance can then be chosen in this AR. [49] presented an excellent overview of this method, while [50] have extended its applicability by proposing an optimization-based targeting method. On the other hand, superstructure methods consider a set of process design alternatives, which includes reactors, such as stirred tank reactors (CSTRs), plug flow reactors (PFRs), cross flow reactors (CFRs), with additional units, such as mixers, splitters, separators, etc. Given a reaction mechanism, kinetic data and physical properties, a mathematical model of the system is formulated and optimization is carried out in order to obtain the sizing and interconnections between the various units, inlet feed rates, stream compositions, and reactor temperatures. The resulting formulation is usually non-convex, due to bilinearities arising from the mass balances and nonlinearities of the reaction kinetics, and hence, a method guaranteeing global optimum currently does not exist. Application of simulated annealing [51], genetic algorithms [52,53], or global optimization techniques, such as the $\alpha$BB algorithm [54] can increase the chance of reaching a global optimum.

Another issue in reactor network optimization using microkinetic models is the computational burden, as the model consists of tens to hundreds of reactions involving several species. While a solution for an idealized reactor (CSTR, PFR or CFR) requires a computational time less than 1 second, the overall optimization is computationally very demanding. Therefore, model reduction techniques described in the previous section can be vital in optimization. Additionally, the optimal reactor network and operating conditions should be physically realizable in the microreactor. Herein lies another opportunity for systems engineering researchers in areas of optimal sensor and actuator placement, and integration of system-wise design and control.

### *6.1. Example: Water Gas Shift (WGS) reaction*

WGS is an important reaction because it reduces the amount of CO – a fuel cell catalyst poison – as well as increases the amount of hydrogen in the reformed gas stream. The overall WGS reaction is:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{4}$$

WGS is a reversible, exothermic reaction; as a result, the CO conversion is equilibrium-limited at high temperatures and kinetically limited at low temperatures. The aim is to determine the optimal temperature profile and feed conditions to minimize the CO content in the effluent. In industrial practice, this is achieved through a two-stage WGS process: a high temperature WGS reactor converts most of the CO to $CO_2$ (and $H_2O$ to $H_2$), whereas a low temperature WGS reactor further reduces the CO content and increases the $H_2$ content of the exit gases.

While the two-stage design of WGS system is a standard practice, not much work has focused on actual optimization of this system, especially in the context of determining an optimum temperature profile. Recently, [55] used the AR method to geometrically determine the optimal reactor design. [56] extended this work to numerically generate the AR, specifically for the WGS reactor. [57], on the other hand, applied the superstructure-based approach to formulate the design problem and used a quasi-Newton technique for optimizing the temperature.

Here, we consider optimization of the temperature and the feed profile for a reaction network shown in Fig. 7. The reactor network consists of *n*-PFRs in series. The CO-rich stream is the feed, steam is fed as the side stream, and an optional recycle is possible. The microkinetic model developed by [27] for WGS on Pt catalyst is used. [58] performed a similar superstructure-based reactor network synthesis for methane acetylization using gas-phase chemistry consisting of 36 reversible reactions and 19 species; however, we are not aware of any reactor optimization work involving catalytic

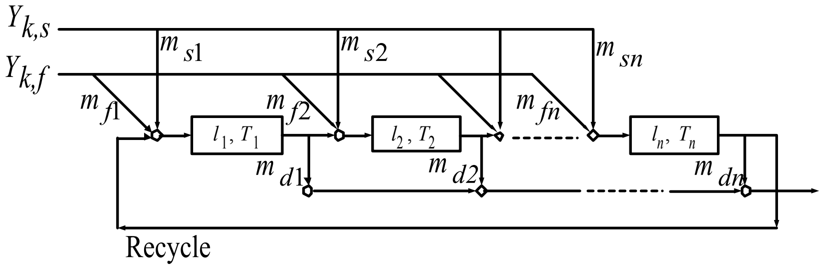

Figure 7: A schematic of the reactor network superstructure consisting of n-PFRs in series.

microkinetic models.

One of the critical aspects in optimization of WGS using microkinetic model is to accurately capture the reaction equilibrium. In the absence of thermodynamic data for the surface-adsorbed species, the scheme proposed in [59] is used to ensure that all our models are thermodynamically consistent. The full model consists of 46 elementary-like reactions. [4] used PCA (principal component analysis) to reduce the model to 18 key reactions. The 18-reaction system was simulated for a wide range of operating conditions; the most abundant reaction intermediate (MARI) and the RDS were identified. Then, small parameter asymptotics was used to derive a 1-step global rate expression. In comparison to commonly postulated Langmuir-Hinshelwood rate expressions, an advantage of this *a posteriori* model reduction strategy is that the rate parameters are physically meaningful, no *a priori* assumptions were made in obtaining the model, the "loss of information" is well characterized and the model, being developed from a microkinetic model, is applicable over a wide range of operating conditions. As the simulation time for the reduced order expression is significantly lower than that for the 46-step mechanism, the reduced mechanism was used for optimization results presented here. Comparison of the results of the full and reduce chemistry models will be presented elsewhere. Note that the reduced expression still accounts for all the important surface phenomena, such as temperature and coverage-dependent activation energies.

Using the reduced-order model, we undertook reactor network optimization in two steps. First, we assumed an isothermal system and performed optimization using a gradient-based (quasi-Newton) optimizer. Based on these results, we were able to simplify the reactor network, as follows: recycle stream was not required since the recycle ratio was equal to or close to 0; the CO-rich stream is fed only at the inlet or PFR-1 (i.e., $m_{fi} = 0 \ \text{for}\, i > 1$); steam may be split over the *n*-PFRs; no intermediate side-draw.

The reactor network optimization problem was thus simplified to the one of optimizing the total reactor length, the temperature, and the feed rate of the side streams for each of the *n* PFRs. The resulting optimal temperature (a local minimum) profile with *n* = 10 reactors, shown in Fig. 8, indicates the expected trend: the temperature is high in the initial reactors, where the CO concentration is higher, and drops significantly as the CO

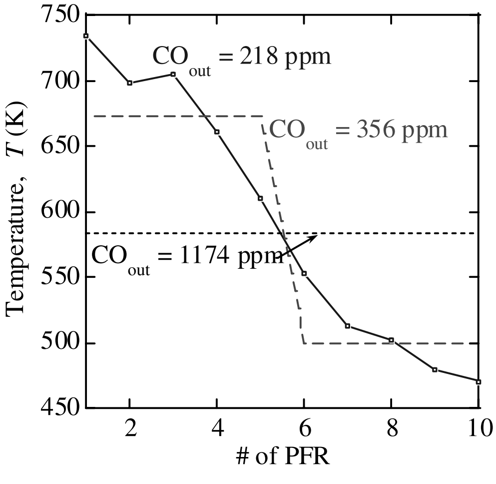

Figure 8: Optimum temperature profile for a reactor network consisting of 10-PFRs in series obtained using a quasi-Newton scheme. The dotted line represents one isothermal reactor and the dashed line represents two-stage WGS reactors. In all cases, total reactor length was 2.0 cm

conversion increases due to the system getting equilibrium limited.

It is interesting to compare the optimization results with that used in industrial practice, and the ones obtained using AR by [56]. There are two different stages in WGS: high temperature stage with $T \sim 700$ K and the low temperature stage with $T \sim 450$ K. The higher limit represents a "break-off" point: an increase in temperature does not result in any significant increase in the reaction rate, but adversely affects the equilibrium conversion. The lower temperature limit is a trade-off between higher equilibrium conversion and a lower rate of reaction. Fig. 8 also provides a comparison between the non-isothermal system, a two-stage system described above, and an isothermal system. In all cases, the total reactor length was 2 cm and 40 sccm feed (dry basis) and 40 sccm steam. The optimized non-isothermal system results in significant improvement over two-stage and isothermal systems.

## 7. Integrated Microchemical Devices: Opportunities for Systems Engineering

In the preceding section, discussion focused on reaction kinetics and on design and optimization of single microreactor(s). Production of power requires integration of reactors, heat exchangers, and separation units, much like in a chemical plant. The characteristic length scales of typical microscale devices are on the order of several hundred microns, and as a result, at high pressures the continuum approximation still holds for the reactor itself. Therefore, the conventional equations of motion and transport are still applicable for the device. Yet, at the catalyst scale, reaction and transport within pores require smaller scale, often non-continuum models, as shown in Figs. 2 and 1 and discussed in the previous sections. So one may ask the question of whether there are any differences between microscale devices and their large-scale counterparts even at the reactor scale. The answer to this is affirmative.

First, due to their small scale the flows in microdevices are laminar and so mixing is slow. Yet one needs to achieve high performance in shorter residence times. This leads to the potential of break through and/or incomplete conversion. Furthermore, small particulates needed to fill a microdevice in order to give high surface area catalyst, cause huge pressure drops, and as a result the fixed bed paradigm for separation or reaction cannot be employed. Moveable, small parts break and can cause bypassing due to settling. These aspects point to the realization that different structures, possibly monolithic-like, need to be explored to overcome issues of mixing, high catalyst area, and pressure drop [60]. Operation is often transient, e.g., turning on and off a laptop, and thus, the catalyst must be active not only at steady state (common industrial situation). In addition, heat transfer must be sufficiently fast (orders of seconds or smaller) to achieve reasonable operation. Hybrid systems, where a small battery is used for start up, followed by a device converting chemical energy to electricity is a process alternative with most promise.

Second, the increase in surface area per unit volume resulting from miniaturization results in an increase of transport rates, and thus, a microreactor has the potential to operate under kinetically controlled conditions. This is a major advantage in terms of process intensification (high throughput with small devices) and the ability to extract intrinsic kinetics from experimental data. However, hot spots could form due to higher rates. Furthermore, surface reactions are favored over gas-phase reactions. This fact has interesting implications for radical quenching of gas-phase combustion chemistry leading to inherent device safety, regarding flame propagation, but also to the inability of making workable gaseous microburners [42]. Heat losses become large, and thus designs that ‘trap’ energy inside the system [61] are highly desirable. The proximity of gas-phase chemistry to walls makes surfaces not only important for carrying out chemistry but the main conduits of heat transfer. As a result, the material makeup of the walls is crucial [62].

Miniaturization, in conjunction with heat losses requires compact, well-integrated designs with a very different layout (flow-sheet) than their large-scale counterparts. The different chemical and heat transfer characteristics found at microscales may render conventional wisdom originating from large scales inapplicable to the design of microdevices [63]. For example, co-currently and counter-currently coupled microreactors (multifunctional devices of carrying endothermic and exothermic reactions on opposite sides of a wall) hardly have any difference in their stability and maximum hydrogen produced when materials are highly conductive [64]. Thus, process design and control of microdevices (lab-on-a chip) need substantial rethinking [65] keeping in mind the aforementioned pros and cons of microchemical devices. Due to the strong coupling of various components, design and control of individual units is unlikely to work; interactions between various units need to be accounted for. This issue is further acerbated because these systems often run in transient operation. This is currently a relatively uncharged territory.

Modeling of these systems needs PDEs, leading to infinite dimensional systems that are not easily amenable for control. Hence, model reduction methods are required to obtain control-relevant models. With the development of novel MEMS sensors and actuators, their optimal placement for estimation and fault diagnostics, and for improving flow and/or temperature control will receive more attention [66,67]. Finally, the shorter time scales, of the order of minutes to hours, make them suitable for "plant-wide" optimization and control schemes.

## 8. Summary and Outlook

With rapid advances in nano- and micro-systems, multiscale simulation and analysis is emerging as a new paradigm in computational science that could facilitate a better understanding of the underlying physics, and enable improved design, optimization and control of these complex systems. The aim of this article was to highlight the progress achieved in this field in the last decade. This emerging field presents new challenges as well as new opportunities, and will benefit from an increased synergism between reaction engineering and process systems engineering communities.

Specifically, this paper discussed the hierarchical multiscale modeling work done in our research group. We demonstrated how the various tools at different scales of the “multiscale simulation ladder” have been used to develop more accurate and physically meaningful microkinetic models that can be applied over a large range of operating and design conditions. Quantum mechanics, molecular dynamics, semi-empirical methods, Kinetic Monte Carlo (KMC), and coarse-grained KMC methods have been put to use to obtain those parameters that are unknown and where experimental data is lacking. System tools, such as parameter estimation, response surface method, identifiability analysis have been applied to improve the quality of models. Model reduction was used to obtain reduced-order models that are useful for tasks, such as CFD simulation/design of reactors, reactor network synthesis, etc.

Process design and control of micro- and nano-scale systems needs careful rethinking since on the one hand system integration, thermal management, and water management are key, challenging issues that await solutions, and on the other hand measurements, sensing, actuation, and control are plagued by the large disparity of scales. Aside from modern applications, the systems community has also to offer lots to the development of multiscale simulation itself in terms of passing optimum information between models at various scales with minimal error, integrating data with models across scales, and developing reduced models. Some of these issues have briefly been touched upon above with examples from the fuel-processing arena and are also addressed in [12-14,68-70].

The low cost of Beowulf clusters renders multiscale simulation a reality. However, multiscale modeling requires substantial intellectual infrastructure, mainly in techniques that span a wide range of scales and is particularly demanding on students. In most cases, such research can be accomplished at a reasonable pace only via collaboration(s). In the long term, the creation of suitable training modules, courses, textbooks, and summer schools is needed for broad dissemination of multiscale modeling.

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## References

[1] NRC, Committee for the Electric Power of the Dismounted Soldier, Energy-Efficient Technologies for the Dismounted Soldier, National Academies Press, Washington DC, 1997.
[2] J. Hallmark, in DOE Fuel Cell Portable Power Workshop, Phoenix, AZ, 2002.
[3] A.C. Fernandez-Pello, Proc. Combust. Inst. 29 (2003) 883.
[4] A.B. Mhadeshwar, D.G. Vlachos, Journal of Catalysis 234 (2005) 48.
[5] M.A. Snyder, D.G. Vlachos, Mol. Sim. 30 (2004) 561.
[6] D.G. Norton, K.W. Voit, T. Brüggemann, D.G. Vlachos, E.D. Wetzel, in Army Science Conference, 2004, p. accepted.
[7] W.M. Yang, S.K. Chou, C. Shu, Z.W. Li, H. Xue, Applied Physics Letters 84 (2004) 3864.
[8] J. Peirs, D. Reynaerts, F. Verplaetsen, Sensors and Actuators A 113 (2004) 86–93.
[9] I.A. Waitz, G. Gauba, Y. Tzeng, J. Fluids Eng. 120 (1998) 109.
[10] I.G. Kevrekidis, C.W. Gear, G. Hummer, AIChE Journal 50 (2004) 1346.
[11] D. Maroudas, in Challenges for the chemical sciences in the 21st century: Information and communications report, National Academies, Washington, D.C., 2003, p. 133.
[12] R.D. Braatz, R.C. Alkire, E. Seebauer, E. Rusli, R. Gunawan, T.O. Drews, X. Li, Y. He, in International Symposium on Dynamics and Control of Process Systems, Cambridge, MA, 2004, p. Paper 96.
[13] P.D. Christofides, AIChE Journal 47 (2001) 514.
[14] D.G. Vlachos, Adv. Chem. Eng. (2005) in press.
[15] S. Raimondeau, D.G. Vlachos, Chemical Engineering Journal 90 (2002) 3.
[16] S. Raimondeau, P. Aghalayam, D.G. Vlachos, M. Katsoulakis, in Foundations of Molecular Modeling and Simulation, AIChE Symposium Series No. 325, 97, 155-158., 2001.

[17] S. Raimondeau, D.G. Vlachos, Journal of Computational Physics 160 (2000) 564.
[18] Y. Lou, P.D. Christofides, AIChE J. 49 (2003) 2099.
[19] Y. Lou, P.D. Christofides, Computers and Chemical Engineering 29 (2004) 225–241.
[20] S. Linic, M.A. Barteau, Journal of Catalysis 214 (2003) 200.
[21] E.W. Hansen, M. Neurock, Journal of Catalysis 196 (2000) 241.
[22] Z.-P. Liu, P. Hu, M.-H. Lee, J. Chem. Phys. 119 (2003) 6282.
[23] A.A. Gokhale, S. Kandoi, J.P. Greeley, M. Mavrikakis, J.A. Dumesic, Chemical Engineering Science 59 (2004) 4679.
[24] S. Kandoi, A.A. Gokhale, L.C. Grabow, J.A. Dumesic, M. Mavrikakis, Cat. Letters 93 (2004) 93.
[25] C.J.H. Jacobsen, A.B. S. Dahl, B.S. Clausen, H. Topsoe, A. Logadottir, J.K. Norskov, Journal of Catalysis 205 (2002) 382.
[26] J.K. Norskov, T. Bligaard, A. Logadottir, S. Bahn, L.B. Hansen, M. Bollinger, H. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xu, S. Dahl, C.J.H. Jacobsen, Journal of Catalysis 209 (2002) 275.
[27] A.B. Mhadeshwar, D.G. Vlachos, Journal of Physical Chemistry B 108 (2004) 15246.
[28] A.B. Mhadeshwar, D.G. Vlachos, Journal of Physical Chemistry B (2005) in press.
[29] S. Raimondeau, D.G. Vlachos, Chemical Engineering Science 58 (2003) 657.
[30] A. Chatterjee, M.A. Snyder, D.G. Vlachos, Chemical Engineering Science 59 (2004) 5559–5567.
[31] A. Chatterjee, D.G. Vlachos, M.A. Katsoulakis, Journal of Chemical Physics 121 (2004) 11420.
[32] A.S. Tomlin, T. Turanyi, M.J. Pilling, Elsevier Sci. J. 35 (1997) 293.
[33] J. Douglas, Conceptual Design of Chemical Processes, McGraw-Hill, New York, 1988.
[34] S.G. Davis, A.B. Mhadeshwar, D.G. Vlachos, H. Wang, Int. J. Chem. Kinet. 36 (2004) 94.
[35] S. Raimondeau, P. Aghalayam, A.B. Mhadeshwar, D.G. Vlachos, Ind. Eng. Chem. Res. 42 (2003) 1174.
[36] E. Shustorovich, H. Sellers, Surface Science Reports 31 (1998) 1.
[37] M.E. Coltrin, R.J. Kee, F.M. Rupley, Surface Chemkin (version 4.0): A FORTRAN package for analyzing heterogeneous chemical kinetics at a solid-surface-gas phase interface, Sandia National Laboratories Report No. SAND90-8003B, Livermore, CA, 1991.
[38] A.B. Mhadeshwar, J.R. Kitchin, M.A. Barteau, D.G. Vlachos, Cat. Letters 96 (2004) 13.
[39] S.Y. Shvartsman, I.G. Kevrekidis, AIChE J. 44 (1998) 1579.
[40] A.B. Mhadeshwar, D.G. Vlachos, Catalysis Today 105 (2005) 162.
[41] R. Jahn, D. Snita, M. Kubicek, M. Marek, Catalysis Today 38 (1997) 39.
[42] S. Raimondeau, D.G. Norton, D.G. Vlachos, R.I. Masel, Proc. Combust. Inst. 29 (2003) 901.
[43] S.R. Deshmukh, A.B. Mhadeshwar, D.G. Vlachos, Ind. Eng. Chem. Res. 43 (2004) 2986.
[44] S.R. Deshmukh, D.G. Vlachos, Ind. Eng. Chem. Res. 44 (2005) 4982.
[45] P.A. Vanrolleghem, M.v. Daele, D. Dochain, Water Res. 29 (1995) 2561.
[46] J. Delforge, A. Syrota, B.M. Mazoyer, IEEE Trans. Biomed. Eng. 37 (1990) 653.
[47] D. Hildebrandt, L.T. Biegler, in, AIChE, New York, 1995.
[48] F.J.M. Horn, in Third European Symposium, Permagon Press, London, UK, 1964.
[49] M. Feinberg, D. Hildebrandt, Chemical Engineering Science 52 (1997) 1637.
[50] L.T. Biegler, S. Balakrishna, in J.L. Anderson (Editor), Advances in Chemical Engineering, Academic Press, New York, 1996, p. 247.
[51] J.C. Cordero, A. Davin, P. Floquet, L. Pibouleau, S. Domenech, Computers & Chemical Engineering 21 (1997) S47.

[52] J.K. Rajesh, S.K. Gupta, G.P. Rangaiah, A.K. Ray, Industrial & Engineering Chemistry Research 39 (2000) 706.

[53] M.W. Deem, in A.K. Chakraborty (Editor), Molecular modeling and theory in chemical engineering, Academic Press, New York, 2001, p. 81.

[54] W.R. Esposito, C.A. Floudas, Journal of Global Optimization 22 (2002) 59.

[55] W. Nicol, D. Hildebrandt, D. Glasser, Computers & Chemical Engineering 26 (2002) 803.

[56] S. Kauchali, B. Hausberger, D. Hildebrandt, D. Glasser, L.T. Biegler, Computers & Chemical Engineering 28 (2004) 149.

[57] A. Jahanmiri, R. Eslamloueyan, Chemical Engineering Communications 189 (2002) 713.

[58] C.A. Schweiger, C.A. Floudas, Industrial & Engineering Chemistry Research 38 (1999) 744.

[59] A.B. Mhadeshwar, H. Wang, D.G. Vlachos, Journal of Physical Chemistry B 107 (2003) 12721.

[60] S.R. Deshmukh, D.G. Vlachos, AIChE Journal (2005) accepted.

[61] P.D. Ronney, Combustion and Flame 135 (2003) 421.

[62] D.G. Norton, D.G. Vlachos, Chemical Engineering Science 58 (2003) 4871.

[63] D.G. Norton, S.R. Deshmukh, E.D. Wetzel, D.G. Vlachos, in Y. Wang, J.D. Holladay (Editors), Microreactor Technology and Process Intensification, ACS, New York, 2005, p. 179.

[64] S.R. Deshmukh, D.G. Vlachos, Chemical Engineering Science 60 (2005) 5718.

[65] A. Mitsos, I. Palou-Rivera, P.I. Barton, Ind. Eng. Chem. Res. 43 (2004) 74.

[66] L.G. Bleris, M.V. Kothare, Ieee Transactions on Control Systems Technology 13 (2005) 853.

[67] C. Antoniades, P.D. Christofides, Computers & Chemical Engineering 26 (2002) 187.

[68] A. Armaou, C.I. Siettos, L.G. Kevrekidis, International Journal of Robust and Nonlinear Control 14 (2004) 89.

[69] M.A. Gallivan, H.A. Atwater, Journal of Applied Physics 95 (2004) 483.

[70] E. Rusli, T.O. Drews, R.D. Braatz, Chemical Engineering Science 59 (2004) 5607.