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# CREATING & USING BIG KINETIC MODELS: MECHANISM TRUNCATION ERROR & OPERATOR SPLITTING

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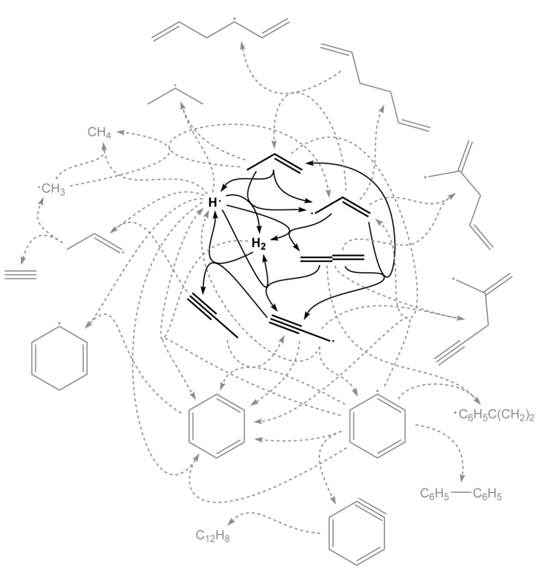
Chemical kinetic modeling for engineering has followed two different tracks. One approach is to treat it as a fitting exercise, to develop a simple model to interpolate limited experimental data. However these simple models are typically not reliable in extrapolation since they do not conform to true complexity of the chemistry.

An alternative approach that might allow more accurate extrapolation is to try to construct a detailed model based on elementary reaction steps which correctly accounts for the complexity of the chemistry. Because of the complexity, detailed models usually contain too many rate coefficient and thermochemical parameters for them to all be determined from the limited experimental data, but these fundamental parameters can be computed using quantum chemistry or estimated by functional group analogy. Since the parameters can be determined before doing any experiments, this approach allows one to make predictions, facilitating computer-aided design of new chemical processes. However, there are serious questions about the quantitative accuracy of these big detailed kinetic models, both whether the parameters are accurate, and also whether the detailed model accidentally omitted an important reaction, e.g. if the model includes only the dark species in the figure,



would the omission of all the grayed species and reactions significantly affect the model predictions? We call the error due to this type of omission “mechanism truncation error”. I will discuss model-construction algorithms which try to reduce this error. Mathematically, a chemical kinetic model is trying to provide the chemical source term $\omega(\mathbf{C},T)$ in the species conservation equations, where **C** are the concentrations, **Y** are the mass fractions, **j** are the diffusive fluxes, and **W** are the molecular weights:

$$\frac{\partial \rho Y_n}{\partial t} + \nabla \cdot \rho V Y_n = -\nabla \cdot j_n + \omega_n W_n$$

But the $\omega$ used in the model is not the true chemical source term because we are not using the true values of the parameters (rate coefficients **k**, equilibrium constants **K**, or activity coefficients $\gamma$) and also because the model omits some of the reactions which actually occur in the system. The omission of reactions is represented by a matrix **Z**, which is a diagonal matrix with 1 on the diagonal if a reaction is included, and 0 if the reaction is omitted. The two sources of error can be defined this way:

$$\omega_{\text{true}}(\mathbf{C},T;\ \mathbf{k}_{\mathbf{true}},\mathbf{K}_{\mathbf{true}},\boldsymbol{\gamma}_{\mathbf{true}}) = \boldsymbol{\omega}(\mathbf{C},T;\ \mathbf{Zk},\mathbf{K},\boldsymbol{\gamma}) + (\text{Parameter error}) \\ + (\text{Mechanism Truncation error})$$

$$\text{Parameter error} = \boldsymbol{\omega}(\mathbf{C},T;\ \mathbf{Zk}_{\mathbf{true}},\mathbf{K}_{\mathbf{true}},\boldsymbol{\gamma}_{\mathbf{true}}) - \boldsymbol{\omega}(C,T;\ \mathbf{Zk},\mathbf{K},\boldsymbol{\gamma})$$

$$\text{Mechanism Truncation error} = \boldsymbol{\omega}(\mathbf{C},T;\ \mathbf{k}_{\mathbf{true}},\mathbf{K}_{\mathbf{true}},\boldsymbol{\gamma}_{\mathbf{true}}) - \boldsymbol{\omega}(\mathbf{C},T;\ \mathbf{Zk}_{\mathbf{true}},\mathbf{K}_{\mathbf{true}},\boldsymbol{\gamma}_{\mathbf{true}})$$

Even if we can construct a sufficiently accurate model for $\omega$, it can be challenging to employ it in reactor engineering simulations, since it contains many state variables. Our approach to that challenge is operator splitting, so that specialized parallel solvers can be used for the stiff chemistry equations in each finite volume, while other solvers are used to handle convection and diffusion. I will discuss an operator splitting method invented by Speth which is particularly helpful for steady-state reactor simulations using very large reaction mechanisms.

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A large number of students and collaborators have contributed to the development and testing of the algorithms for reducing mechanism trunctation error in the RMG software over the last 15+ years, I have learned a great deal from working with them and they continue to teach me every day. Most of the RMG development was funded by the US Dept. of Energy. The operator splitting method was developed by R.A. Speth, and tested by Alan Long with financial support from ExxonMobil

# Multi-scale Coarse-grained Models for Simulation of Coupled Homogeneous-Catalytic Reactions in Monoliths

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Monolith reactors are widely used in catalytic after-treatment, catalytic combustion and partial oxidations. In most applications, the washcoat containing precious group metals is deposited as a single layer on the channel walls (schematic shown in Figure 1). In recent years, multi-functional monolith reactors consisting of two or more washcoat layers with different functionalities are also used. Examples include dual layered selective catalytic reduction (SCR) units; hydrocarbon (HC) trap and an oxidation layer; and diesel oxidation catalysts (DOCs) with two different oxidation layers. In these systems, the exhaust gases (including the reactant, product and carrier gases) flow through the channel in axial direction and diffuse into the washcoats where they are trapped (adsorbed) or react. In the automobile exhaust treatment applications, the monolith reactors operate under highly transient conditions. Therefore, the development of coarse-grained(reduced order) models for these systems is important for various control and optimization algorithms related to fuel efficiency and real time implementation of emissions constraints. These reduced order models have also other advantages such as speed-up of the transient reactor calculations by several orders of magnitude, parametric studies and bifurcation analysis, and estimation of kinetic and transport parameters from a limited number of macroscopic experimental observations (or the solution of the so called inverse problem). In addition, they facilitate the incorporation of the model in larger scale process and optimization schemes.

Because of the above mentioned and other applictaions, several researchers have developed reduced order models for monolith reactors. For example, based on the approach proposed by Balakotaiah [1], two-mode model for real-time simulation of a single-layered monolith was developed by Joshi et al. [2]. In recent years, more accurate reduced order multi-mode models were also developed for single-layered monoliths with global and micro-kinetics ([3], [4]). Mozaffari et al. [5] extended the work of Joshi et al. [2] to dual layered monoliths to obtain a simplified model by utilizing kinetic dependent transfer coefficients. More recently, we developed multi-scale multi-mode models for monoliths with multiple-layers for multicomponent systems [6], which is more accurate and can lead to exact solution when kinetic-dependent transfer coefficients are utilized.

In the current work, we apply the multi-scale averaging procedure developed in [6] to a multi-layered catalytic monolith reactor for non-isothermal case coupled with homogeneous reactions in fluid phase. We provide the reduced order model for the coupled heat and mass-transfer processes with chemical reactions in multi-mode form, containing interfacial heat/mass fluxes as well as phase/velocity averaged temperatures and concentrations. These models are most suitable for bifurcation analysis and solving inverse problems for estimating transport/reaction parameters. Finally, we give physical interpretations of the various inter- and intra-phase transfer coefficients, discuss the limiting cases and illustrate the use of multi-scale multi-mode reduced order models with examples.

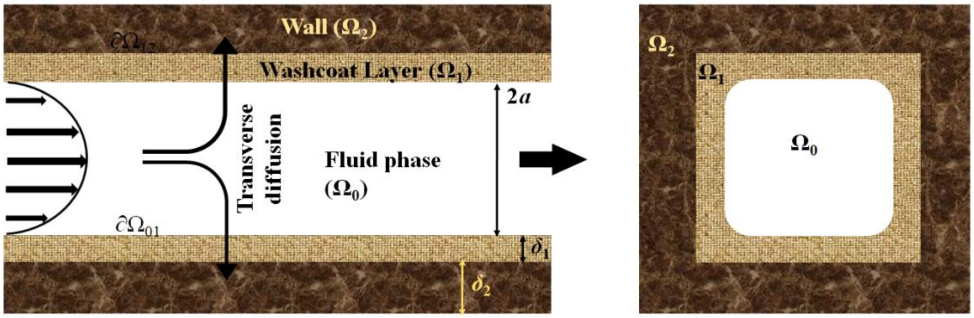

Figure 1: Schematic of a catalytic monolith with a single washcoat-layer and a wall

**Key Words**: Multi-scale modeling, Lyapunov-Schmidt reduction, Multi-phase reactors, Transfer Coefficients, Real Time Simulation, Multi-layer monolith.

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# A penalization method for the direct numerical simulation of low-Mach reacting gas-solid flows

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Gas-solid flows are encountered in a variety of natural phenomena and industrial applications. Fluidized bed reactors are widely used in the chemical industry as they allow continuous solids processing and high mass and heat transfer rates. The simulation of industrial scale fluidized bed reactors remains challenging with billions of solid particles in motion in the reactor. In the past decades, different approaches have been developed to model complex multi-scale and multi-phase reacting flows. The Two-Fluid Model (TFM), which describes both the gas and the solid phases as continua, is currently very popular due to its relatively low computational cost. The Discrete Element Model (CFD-DEM) or its coarse-grained version in which each particle, respectively group of particles, is tracked in a Lagrangian manner has gained attention in recent years due to the increased computational power and parallel processing capabilities. However, both TFM and DEM type models depend on closure laws for interfacial mass, heat and momentum transfer. Direct Numerical Simulation (DNS) turns out to be a powerful tool for extracting closure laws starting from the fundamental principles for mass, momentum and heat transfer.

In recent years, different DNS methodologies for particle-resolved simulations have been investigated, mostly based on the Immersed Boundary Method (IBM) originally developed by Peskin [1]. The direct forcing method introduced by Mohd-Yusof [2] and later improved by Uhlmann [3] allows a better numerical treatment of rigid body problems and is therefore very popular in the fields of particulate flows. DNS-IBM was then applied by several research groups to predict fluid-particle mass, momentum and heat transfer rates [4]–[8].

Among immersed boundary methods, the penalization method developed by Arquis and Caltagirone [9] models solid obstacles as porous media with close to zero porosity. Originally used for fluid-structure interaction, this method has been scarcely investigated for the study of heat and mass transfer problems in reactive gas-solid flows.

The present study combines the penalization method to account for the presence of the solid phase with the low-Mach number assumption for the gas phase. Indeed, strong thermal effects induced by chemical reactions can induce non-negligible density gradients at the surface of solid particles and affect interfacial transfer laws. The low-Mach number assumption is of high interest for gas-solid reactive flows in that it allows density fluctuations while removing the constraint on the time step imposed by the speed of sound in fully compressible flows. Here, we extend the methodology of Lessani et al. [10] for low-Mach number flows in order to incorporate the penalization of the solid phase for momentum, heat and species transport. Different reaction scenarios are investigated: heat consumption/production and gas expansion/compression. Finally, a comparison is established with the incompressible version of the penalization method to assess the impact of density fluctuations in view of building new closure laws for gas-solid flows.

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# Thermodynamically consistent kinetic model for the naphtha reforming process

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The prediction and application efficiency of kinetic models for the complicated reaction systems, such as petrochemical process, is defined by optimal relation between the level of reaction and reactants detailization and the number of kinetic parameters in the model. Earlier [1], we have proposed the approach based on reasonable grouping of reactants and reactions into homologue groups with description of difference between individual reaction rates within the group by account of thermodynamic potentials (first of all, free Gibbs energy of corresponding reactions) in the value of the apparent activation energy of the given reaction. Particularly, it was shown that the rates of aromatization of all normal paraffins into corresponding alkylbenzenes might be described by one common equation:

$$W_j = k_0 \exp\left(-\frac{E+\beta\Delta G_j}{RT}\right)\left(P_{n/i-Pi} - \frac{P_{ARi}P_{H_2}^4}{K_{Pj}}\right)$$

where $k_0$ – pre-exponent, $E$ – activation energy, $\Delta G_j$ – free Gibbs energy for $j$-th reaction, $P$ – partial pressures of reactants, $K_{pj}$ – equilibrium constant for $j$-th reaction, $\beta$ - empiric coefficient. Thus, we may describe the rates of 5 individual reactions (for $C_6$-$C_{10}$ n-paraffins) using only 3 kinetic parameters to be defined from experiments ($k_0$, $E$ and $\beta$) instead of 10 parameters (5 pairs of $k_0$ and $E$ for each reaction).

The similar approach may be applied to aromatization of iso-paraffins and hydrodecyclization of naphtenes, also providing the significant decrease of number of required kinetic parameters.

At the current stage the research was focused on the detailization of the earlier proposed model to provide better description quality, namely:

- the kinetic scheme of paraffins aromatization was improved, giving the way to use one kinetic equation for both n- and iso-paraffins conversion to alkylbenzenes, applicable for all paraffins $C_6$-C11 and for a wide temperature range (Fig.2);

- more detailed scheme was proposed for conversion of naphthenes;
- much more detailed scheme was proposed for paraffins hydrocraking reactions; the approach, based on the description of individual hydrocracking reactions rates for different individual paraffins with account of dissociation energy of the corresponding C-C bonds, was applied;
- much more detailed scheme was proposed for paraffins isomerization reaction, involving separate description of isomerization reactions of carbon chain branching and alkyl radical shift types.

All this has led to significant detailization of the reaction scheme (230 individual reactions belonging to 8 reaction groups instead of 144 and 219 reactions in our previous models), but the number of kinetic parameters to be identified from experimental data increased insignificantly (26 instead of 22), thus keeping the overall simplicity of the model.

As a result, the proposed model significantly exceeds all earlier known naphtha reforming kinetic models [2] in the ratio between the system detailization level and model complexity (fig.1).

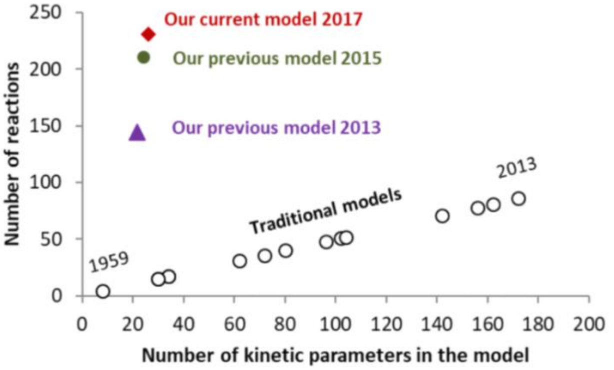

***Fig. 1.*** *Ratio between the reaction system detailization level and model complexity for pro-posed model and conventional naphtha re-forming models (according to data from [2]).*

In some respect, the presented method in some respect echoes with the “single events” approach [3], though, of course, possible connection and competition between them requires further studies and discussions.

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# Reaction rate oscillations in a catalytic flow reactor operating in a mass-transfer limited regime.

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Recently, the Planar Laser-Induced Fluorescence (PLIF) was developed for 2D and 3D imaging of the gas phase close to an operating single crystal catalyst [1]. This gas detection technique can spatially resolve gases close to a sample surface in real time. It was applied for the CO oxidation reaction on Pd(100) at near ambient pressures in excess of oxygen and the temporal changes in the gas phase were visualized during the oscillations [1]. The main goal of this work is to present a reactor model capable of reproducing the experimental PLIF results concerning the spatial distribution of CO and $CO_2$ in the catalytic reactor, including the oscillatory behaviour on Pd(100) surface using well-known Sales-Turner-Maple (S.T.M.) model [2]. The reactor model takes into account the convection and diffusion processes. Simulations show that at high temperatures the reaction proceeds in the mass-transfer limited (MTL) regime, more specifically, the reaction rate is limited mainly by the gas-phase diffusion of CO.

The catalytic reactor is represented by a rectangular cuboid of L × W × H size. The catalyst is located in the bottom of the reactor similar to the work [1]. The model is based on the following system of 3D convection-diffusion-reaction equations:

$$\frac{\partial C_k}{\partial t} = -\mathbf{u}\nabla C_k + \nabla\left[D_k \nabla C_k\right] - W_k^{cat}, \qquad (1)$$

where $C_k$ are the concentrations in the gas phase ($k = 1,\dots,4$ for $O_2$, CO, $CO_2$ and Ar, respectively), $\mathbf{u}$ is the gas velocity, $D_k$ are the diffusion coefficients. The gas-phase temperature $T_g$ is assumed to be constant; the partial pressures are calculated as $P_k = RT_g C_k$. Eq. (1) is supplemented by a Robin-type boundary condition with the inlet partial pressures $P_k^{in}$ at the inflow boundary (left side, x = 0). The mass flux of the individual species is equal to zero at the outflow boundary (right side, x = L), as well as at the top (z = H) and bottom sides (z = 0, except the catalyst area) of the reactor.

The reaction terms $W_k^{cat}$ are non-zero only in a specific region where a catalyst is located. The Eq. (1) is coupled with the space-distributed kinetic model which is represented by the S.T.M. model for the adsorbate coverages $\theta_O$, $\theta_{CO}$ and $\theta_{ox}$. The S.T.M. model is based on the Langmuir–Hinshelwood mechanism and considers the surface oxide formation. For numerical solution of Eq. (1) the finite-difference approximation is applied. Using the relation of Fuller−Schettler−Giddings and the Wilke equation, the diffusion coefficients $D_k$ are calculated at each mesh point, given that molecular diffusivities are dependent on the local gas pressure.

Figure 1 shows the spatial distributions of CO and $CO_2$ calculated for the high-activity state during the oscillations at $P_{O2}^{in} = 120$ mbar, $P_{CO}^{in} = 6$ mbar. In this way the formation of a $CO_2$ cloud or boundary layer around the catalyst is visualized. Such images are typical for the MTL regime [1]. The CO partial pressure in the boundary layer is about 2.5 mbar, but the total conversion of CO is ~10% only. The low-activity state is characterized by practically homogeneous distribution with $P_{CO} \approx P_{CO}^{in}$, $P_{CO_2} \approx 0$.

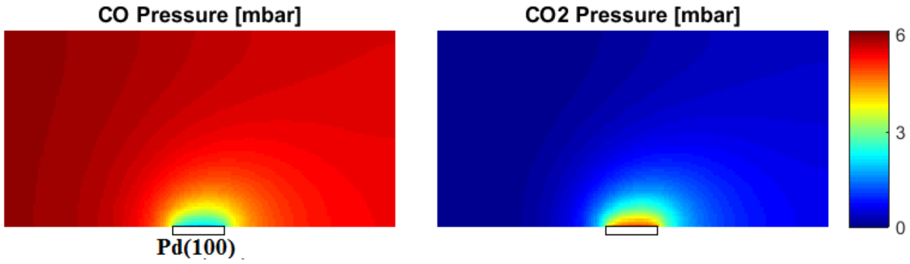

Fig. 1. Spatial distributions of CO and $CO_2$ for the high-activity state during the oscillations. Reactor: 3×3×1.5 $cm^3$. Catalyst: 4×4 $mm^2$; $T_{cat}$ = 523 K. Inlet flow: $F = 10^{-5}$ $m^3$/s; $T_{gas}$ = 300 K; $P_{O2}^{in} = 120$, $P_{CO}^{in} = 6$, $P_{Ar}^{in} = 24$ mbar.

In summary, the developed mathematical model based on the S.T.M.-kinetic mechanism coupled with a detailed model of the mass-transfer in the reactor successfully simulates the spatial distributions of CO and $CO_2$ during oscillations in CO oxidation over Pd(100) obtained by the PLIF method.

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# Modeling the transition from oxidative coupling to partial oxidation of methane by Ir-doping on $La_2O_3/CeO_2$ nanofiber catalyst

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Oxidative coupling of methane (OCM) is an important process to directly convert methane to higher hydrocarbons in the presence of oxygen. OCM mainly produces the desired product ethylene with some side products such as acetylene, propene, and $CO_x$. La-based catalysts are considered potentially viable to commericalize the OCM process and nanostructured $La_2O_3/CeO_2$ catalysts showed superior performance over traditional La-based catalysts. However, the latter nanostructured catalysts still could not satisfy the yield and selectivity of $C_2+$ to achieve commercial viability. Noon et al.[1] synthesized $La_2O_3/CeO_2$ nanofibers which could achieve $C_2+$ selectivities and yields of up to 70% and 18%. However, by doping increasing amounts of Ir up to 1 wt%, the products shifted from OCM, mainly $C_2$, to partial oxidative of methane (CPO), which is synthesis gas[2]. This demonstrated the possiblity of a new CPO mechanism correlated with OCM, which was different from previous literature. The present study investigates the chemical kinetics and mechanisms for both OCM and CPO in order to further understand this transition process. This work proposes a detailed reaction mechanism describing this transition process dependent on the amount of Ir doping.

The model is developed by combining OCM and CPO mechanisms from various literature. Each reaction is analyzed to validate the mechanism based on the experimental results of spatial concentration and temperature profiles with different amount of Ir doping. The results could provide new insights correlating both OCM and CPO under their complex reaction chemistry.

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# Tomography based simulation of reactive flow at the micro-scale: Particulate filters with wall integrated catalyst

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### Introduction

Due to the need for high contact area, most catalytic systems exhibit a micro-scale structure. The standard simulation approach is to not resolve this micro-scale structure which is then described in terms of volume averaged homogeneous model equations [1]. Today, micro-scale geometries can be routinely obtained by X-ray tomography. In this contribution, the application of tomography-based micro-scale reactive flow simulation is demonstrated for the reactive flow in the pores of a particulate filter wall with integrated catalyst (washcoat). It is shown that micro-scale transport effects have a significant effect on the overall catalyst performance.

### Simulation of the filter wall

A wall segment of a catalyzed particulate filter was analyzed by X-Ray tomography with a spatial resolution of ~1.4 µm and each volume element was assigned as either pore, substrate or washcoat, where only in the latter the reaction is taking place. The flow field and the concentration profiles were then computed using the PoreChem simulation code [2], assuming a first order reaction in the washcoat. The left side of Figure 1 shows the resulting flow field through a filter wall segment. The conversion in the filter wall was compared to a homogeneous model with the same dimensions and catalyst content, see right side of Figure 1.

### Results and Discussion

It was found that the conversion in the pore network is lower than predicted by the homogeneous model, indicating the presence of some kind of in-pore transport limitation. Potential explanations are flow channelization through bigger pores leading to a broadening of the residence time distribution or diffusion limitations within the washcoat. It was found that in our case the reduced conversion can almost entirely be attributed to diffusion limitations in the wall integrated washcoat. If the diffusion in the washcoat was described by a standard effectiveness factor model with the effective washcoat diameter fitted to the results of the full pore scale simulation, a very good agreement between the full simulation and the homogeneous model was found, see right side of Figure 1. The effective washcoat diameter obtained by this fit is surprisingly large, compared to the apparent size of the washcoat particles. This can be explained by the limited accessibility of the washcoat due to the confinement in the pore structure.

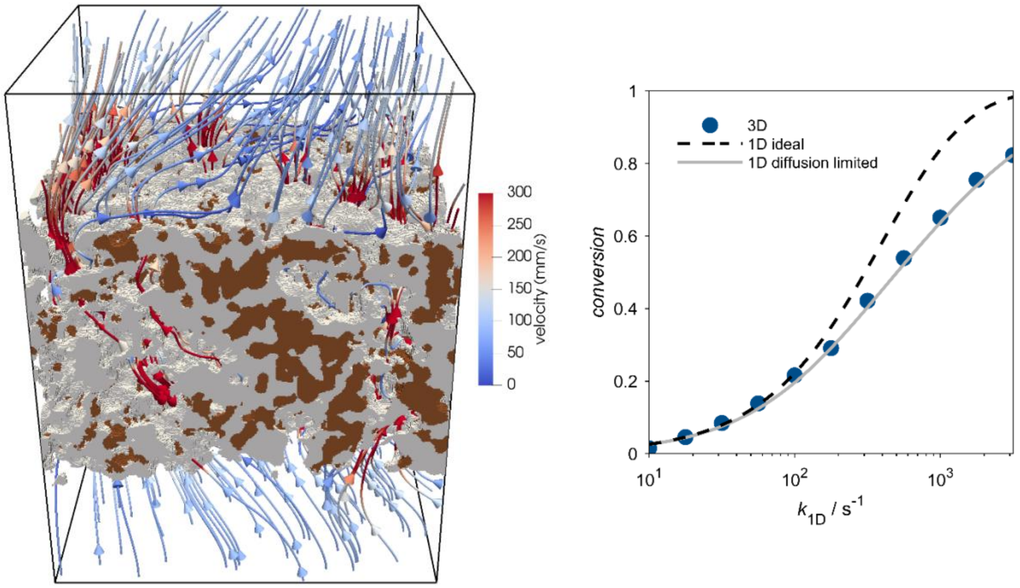

**Figure 1.** Left: section of the filter wall structure (490×640×490 µm); substrate (grey), washcoat (brown). Lines show the flow field. Right: conversion of the different models versus the reaction rate.

### Conclusions

In the shown case, micro-scale transport phenomena have significant effect on the overall performance, which would not have been captured by conventional homogeneous models. The result demonstrates the potential of tomography-based simulation for micro-scale catalyst design.

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# PARAMETER ESTIMATION: A BRUTE AND A SMART METHOD

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Given some kinetic measurements of species concnetrations in a chemical system the fundamental problem is to create a mass action type kinetic model and find its parameters (most often: reaction rate coefficients or Arrhenius parameters). We propose a method for automatic model selection and a method for finding good initial estimates for the parameters, again automatically.

## Automatic model construction and selection

As a first step we fix the number of species (this may be the number of species measured or larger). Next, we generate all the combinatorically conceivable and chemically acceptable reaction steps (e.g. those with a kinetic order not higher than two, conserving mass, reversible, not like X → X, or 2X → 2X, 2X → 2Y, etc.). If the number of species is 2, then the following reaction steps remain:

$$\{X \leftrightarrow Y,\ X \leftrightarrow 2\,Y,\ Y \leftrightarrow 2\,X,\ 2\,X \leftrightarrow X + Y,\ 2\,Y \leftrightarrow X + Y\}.$$

Then, we form sets of reaction steps which we call reaction networks (or, shortly: reactions). From these five steps one can form three two-step reactions which are also mass conserving as follows.

$$\{\{X \leftrightarrow Y,\ 2\,X \leftrightarrow X + Y\},\ \{X \leftrightarrow Y,\ 2\,Y \leftrightarrow X + Y\},\ \{2\,X \leftrightarrow X + Y,\ 2\,Y \leftrightarrow X + Y\}\}.$$

Now assuming constant temperature and volume and mass action type kinetics we fit all the obtained reactions (one after another) to the measured concentrations and compare the results using some measure of goodness of fit, like AIC, BIC (Akaike Information Criterion, Bayesian Information Criterion), and present the best fitting reaction to the chemist for further investigations.

We only estimate those reaction rate coefficients which are independent in the sense that they cannot be concluded from detailed balance, a principle which we also assume to be valid in these investigations. We shall also show how the method works when not the concentrations themselves but a function or a functional of them (e.g. period in an oscillatory reaction) are measured.

## Fitting models starting from automatically calculated initial estimates

Models linear in the parameters (even if they are nonlinear in state variables) are easy to fit to measured data. The real problem starts when the model is nonlinear in the parameters as e.g. the sum of two exponentials, or the solution of a (no matter how simple) differential equation. (Cases when the model is linearizable---like the function $t \to Ae^{Bt}$---are not really better, classical linearization methods even mislead the researcher.) The success of the art (and not pure science) of parameter estimation in the nonlinear case heavily depends on the initial estimate of the parameters. (Chemically realistic bounds are also of help, although technically they may mean a nuisance.)

To get a good initial estimate one can utilize the intuitively clear fact (what can formally be proven) that although the concentration vs. time curves in kinetic models are almost never linear functions of the parameters, but the right hand side of the induced kinetic differential equation of a reaction is [1,2]. The estimating process then goes on from the initial estimate obtained using this speciality of the right hand side. We show on a few characteristic examples (Lotka-Volterra reaction without diffusion, Fisher equation with diffusion, Belousov-Zhabotinsky reaction with diffusion) with simulated data how this fact can be used to start from a good initial estimate and arrive at a good final estimate. The method can be extended to cases when only some of the parameters influence linearly the right hand side, or when we have compound parameters (e.g. Arrhenius form in non-isothermal systems) [4].

## Methods

All the calculations from combinatorics to estimations are based on our program package ReactionKinetics [3,5] written in the Wolfram language.

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# Towards online redesign of steady state experiments for the identification of kinetic models in flow reaction systems

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Continuous flow microreactors are attracting attention as excellent laboratory devices for performing precise reaction kinetic studies with minimum time and materials [1]. With the emergence of model-based design of experiments (MBDoE) techniques [2] for designing highly informative experiments, enabling the quick development and assessment of deterministic process models, there is now great scope for using the technique online to identify the reaction kinetics in fully automated continuous flow microreactor platforms [1]. This is possible by online model-based redesign of experiments (OMBRE) techniques that allow to exploit the information from an experiment as soon as it is available by updating the experimental settings while the experiment is still running. While the OMBRE technique has been successfully applied for the online redesign of dynamic processes [3], no OMBRE technique has been applied to steady-state processes.

In this work, an optimal strategy for the online redesign of steady state experiments is specifically proposed to identify the kinetic models with a precise estimation of the kinetic parameters in the case study of sulfuric acid catalyzed benzoic acid esterification reaction in an automated continuous flow microreactor.

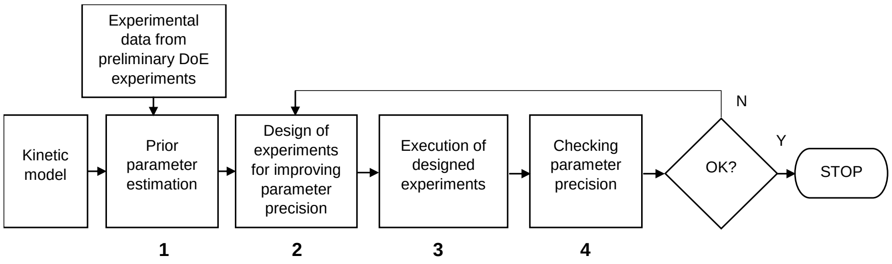

**Figure 1.** Sequential MBDoE procedure for improving parameter precision.

The sequential MBDoE procedure for improving parameter precision is illustrated in Figure 1. The model adequacy test followed by a prior parameter estimation (step 1) from preliminary DOE experiments was used to identify first order kinetic model for the benzoic acid esterification reaction. Further, a sequence of five steady state experiments ($E_1$ – $E_5$), aiming at improving the precision in the estimation of kinetic parameters (activation energy and frequency factor), is designed by solving a single optimization problem (see step 2). This is followed by the execution of designed experiments (step 3) and the statistical assessment of the estimates (step 4). The procedure is iterated until a statistically satisfactory estimation of kinetic parameters is achieved. In this work, a strategy is proposed for the online redesign of steady state experiments by modifying step 2 and 3 and is illustrated in Figure 2.

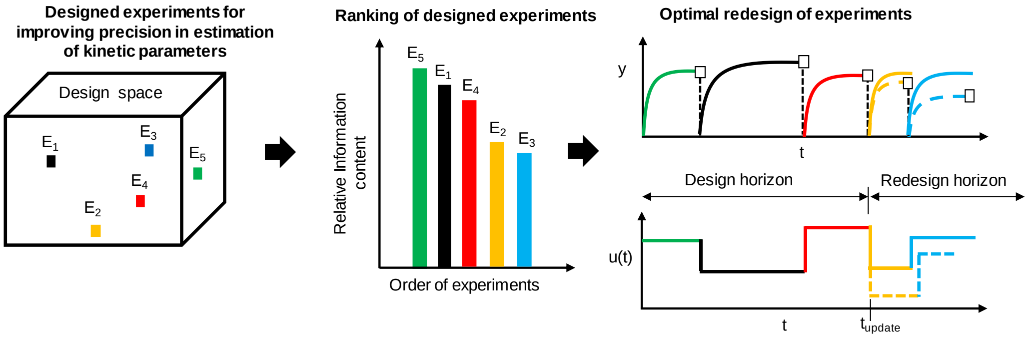

**Figure 2.** Proposed methodology for the optimal redesign of steady state experiments.

In the proposed strategy, the designed experiments ($E_1$ – $E_5$) are ranked based on the relative information content available with individual experiments [4]. The information available from an experiment is quantified in terms of a metric of expected Fisher Information Matrix (FIM) evaluated at the steady state conditions. Finally, the designed experiments are performed following the order of their relative information content. Those experiments which are not contributing much to the information contained in the experimental sequence ($E_2$ and $E_3$) are redesigned (shown in dotted lines) by updating the information from $E_5$ and $E_1$ while $E_4$ is processing. The online framework for redesign of steady state experiments was implemented in the Python language and successfully integrated in a platform for the online identification of kinetic models of benzoic acid esterification.

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# OCM CATALYSTS ASSESSMENT: CLUSTERING TECHNIQUES FOR THE DESIGN AND ANALYSIS OF NUMERICAL EXPERIMENTS

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Ethylene production via Oxidative Coupling of Methane (OCM) has represented a critical challenge in the field of heterogeneous catalysis for the last 35 years and is still an active and engaging research field [1]. OCM catalyst development has been extensively explored both from the experimental and computational point of view. Nevertheless, a 30% $C_2$ hydrocarbons ($C_2H_4$ + $C_2H_6$) yield, commonly considered to be the threshold for an industrially-viable OCM process implementation, has rarely been achieved in fixed-bed reactors, among others due to the high number of variables involved in the catalyst composition optimization [2]. The aim of the present work is to develop a new simulation methodology which can enable the assessment of the performances of a broad variety of OCM catalytic materials. This goal has been pursued by applying so-called clustering techniques [3] to both the design and the interpretation of OCM numerical experiments, with the ultimate objective of providing guidelines for real-life catalyst design.

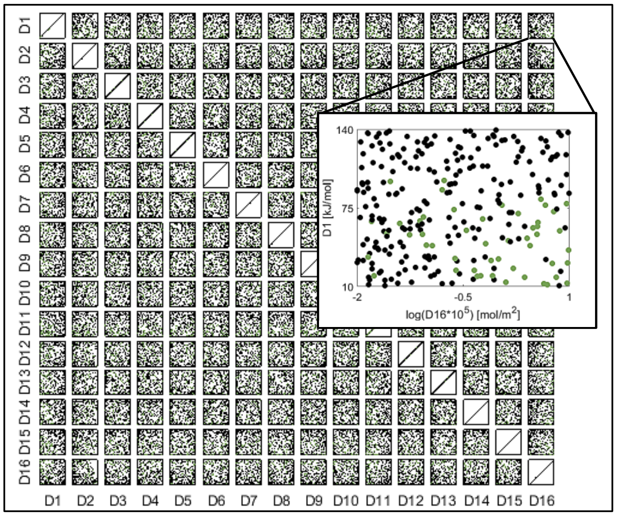

*Figure 1. Virtual OCM catalysts library, represented by the scatterplot matrix of the 16 catalyst descriptors included in the microkinetic model. The zoom reports the scatterplot of D1 vs log(D16·$10^5$). The green dots indicate the catalysts of the a posteriori determined green cluster in Figure 2; the black dots indicate all the other catalysts.*

The numerical 'set-up' used in this work embodies the reactor and microkinetic model as previously developed within our research group [4]. A library of 240 virtual OCM catalysts has been 'tested'. Each catalyst in the library is represented within the model via 16 chemical properties, such as chemisorption enthalpies, initial sticking coefficients, density of active sites. These properties are denoted as 'catalyst descriptors' and account for the impact of the catalyst properties on the kinetics of the elementary steps occurring on the catalyst surface [4]. The library, shown in Figure 1 via a scatterplot matrix of the catalyst descriptors (D1-D16), has been generated via the Fast Flexible space-Filling (FFF) method, a Design of Experiments (DoE) technique based on hierarchical clustering [5]. In the present example, the same operating conditions for the numerical experiments as those reported by Kondratenko et al. [6] have been selected, to allow a straightforward comparison of our results with theirs. The virtual (simulated) and real (experimental [6]) catalysts are grouped based on their catalytic performances at the reactor outlet ($CH_4$ conversion and $C_2$ selectivity and yield) via the k-means++ clustering algorithm [7]. The obtained clusters are reported in Figure 2, together with the iso-yield curves. It is evident that no experimental data can be found in the outperforming region of the plane (green cluster), while the cluster of simulated catalysts with intermediate performances (red cluster) is the one which better reproduces the experimental data. Nonparametric statistics is used for a comparative analysis of descriptor distributions associated to the ‘realistic’ red cluster and the ‘outperforming’ green one, and for correlation analysis between the descriptors within each cluster. The identification of the key descriptors which discriminate among the clusters, such as D1 (reaction enthalpy of H-abstraction from $CH_4$) and D15 (initial sticking probability of $C_2H_4$), leads to a deeper understanding of the kinetically-relevant features of real catalysts and of how those may be improved to effectively achieve the outstanding simulated performances leading to $C_2$ yield ≥ 30% in real life.

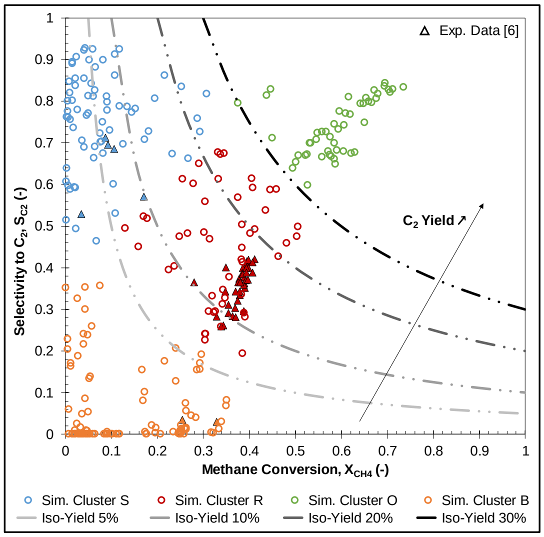

*Figure 2. Simulated (circles) and experimental (triangles) catalytic performances of OCM catalysts tested in the operating conditions reported by Kondratenko et al. [6]. Different colors indicate the different clusters obtained via k-means++ algorithm.*

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# MACHINE LEARNING FOR EFFICIENT AND CONTINUOUS RETROSYNTHETIC PRODUCT DESIGN: A NOVEL REACTION IDENTIFIER

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When organic chemists identify a useful chemical compound — a new drug, for instance — it's up to chemical engineers to determine how to mass-produce it. There could be a dozen different sequences of reactions that yield the same end product. But some of them use cheaper reagents and lower temperatures than others, and perhaps most importantly, some are much easier to run continuously. Key is identifying how reactants are transformed into products and how cheminformatics and machine learning can assist with this task. Typically a vector representation of chemical 'objects' is required in combination with machine learning in (organic) chemistry [1-3]. For accurate results, these representations should be unique to the object they attempt to represent. For molecules a typical approach is the use of molecular fingerprints, which readily translate a molecular graph into a binary vector [4]. A similar single-step approach is not possible for a reaction. Several methods have been applied, all using the product and reactant fingerprints in some way, for example using the difference between the reactant and product fingerprints [5]. While they give a fairly unique description of a single reaction and capture important characteristics of that reaction, they fail at grasping the high level of similarity between reactions that follow the same general reaction template. In cases where the reaction itself is used as input to a neural network, one desires to pass information on the reaction mechanism to the network. This implies that the input for two reactions that follow a same template should be, at the very least, highly similar. To tackle this issue, a new reaction encoder is devised, making use of the vast amount of reaction data available from the Reaxys® database. Using ~15000 templates with the largest number of reaction examples, a network is trained to link reactant and product fingerprints to a reaction fingerprint that is derived from the reference reaction for that template. This reference reaction is derived from the SMIRKS representation of the considered template, as illustrated in Figure 1. The result is an identifier that contains information on the reaction mechanism and that is the same for the reactions that follow this mechanism. The new algorithm is implemented in an algorithm that assesses the likelihood that it is possible to carry out a given reaction with a given set of reaction conditions in continuous synthesis. This algorithm will also provide the set of reaction conditions it considers to be most feasible in continuous flow, for the considered reaction.

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### Figures

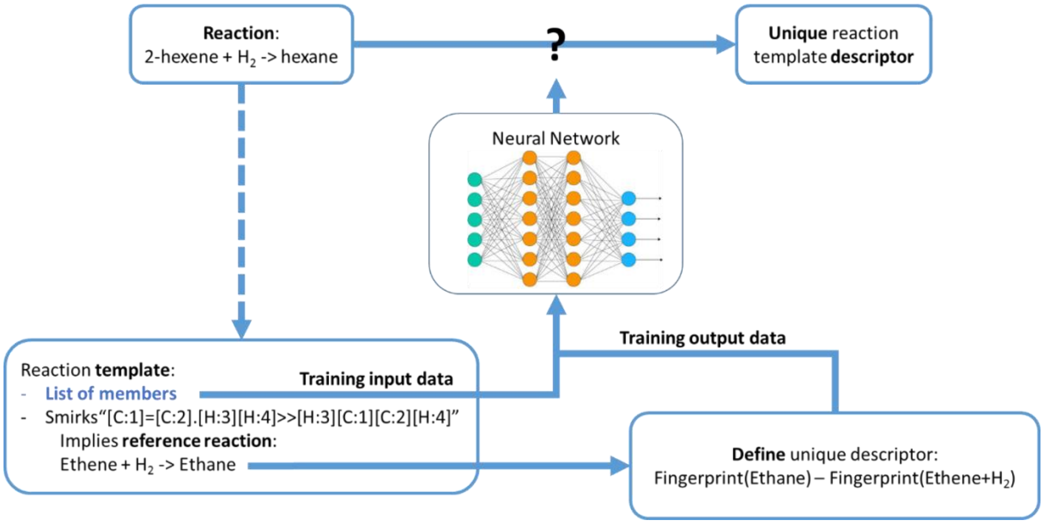

*Figure 1: Conceptual representation of the reaction encoder.*

# AN ARTIFICIAL NEURAL NETWORK APPROACH TO CLASSIFY CHEMICAL REACTION TYPES FROM EXPERIMENTAL DATA

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Chemical reaction kinetics are typically modelled as systems of differential and algebraic equations where the appropriate reaction mechanism is expressed in mathematical form through a set of reaction rate equations. In general, however, many chemical species may be present and many potential reactions may occur in the system, making the construction of an appropriate model structure extremely challenging. Despite the significant effort of many scientists in the area of model identification [1, 2], a robust and systematic approach to kinetic modelling is yet to be proposed and the model construction activity still relies on the experience of researchers for interpreting and extracting information from the experimental data.

Machine learning technology has been demonstrated to be an invaluable tool in supporting the extraction of patterns, even out of vast unlabelled datasets. Artificial Neural Networks (ANN) in particular have found successful application in many fields of artificial intelligence, including image classification and speech recognition [3]. Applications of ANNs in the field of reaction engineering are also available in the literature [4]. These represent attempts of using ANNs as black-box regression models for describing the behaviour of some physical quantities of interest in the reacting system. The main drawback in the current applications of ANNs in reaction engineering is that their training from experimental data does not provide any information on the internal mechanistic nature of the reaction dynamics.

In this work, the possibility of using ANNs for detecting kinetic patterns from experimental data and supporting the construction of mechanistic kinetic models is explored. A simplified diagram representing the proposed conceptual framework is given in Figure 1. The procedure starts from an *in-silico data generation stage*. At this stage, virtual experimental data is generated by employing different model structures (selected from a user-defined library) with randomly generated kinetic parameters.

This stage is run a number of times to obtain a sufficiently vast data set, which covers all the possible model structures and the range of possible values for the uncertain kinetic parameters. The following step involves the training, validation, optimisation of the ANN and, eventually, testing of the ANN classification performance [5]. The proposed approach is demonstrated on a simple three-component reacting system simulated in batch, where the modelling space involves 8 possible kinetic model structures. In the presented case study, optimised ANNs achieved reaction classification accuracies above 95%, provided that the available experimental data is sufficiently informative.

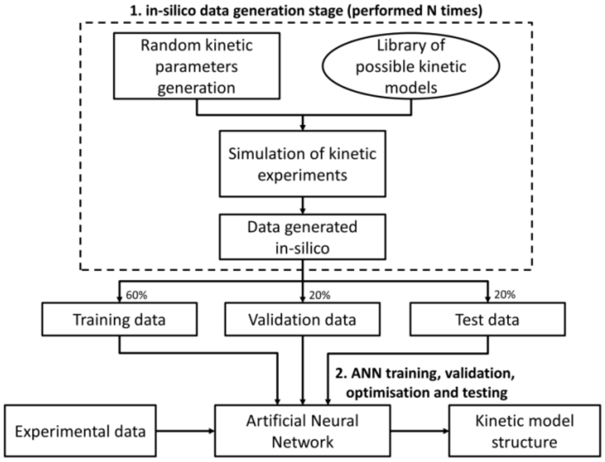

Figure 1: Proposed framework for ANN-based reaction type classification.

The presented study demonstrates the possibility of employing effectively ANNs technology for modelling human-level reasoning in the mechanistic modelling task. It is an objective of future work to extend and test the proposed approach to more complex cases (more components in the system and more possible reaction mechanisms), where the amount of information to process from the data is further beyond human reach.

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# Analysis of Radial Effects in Non-Isothermal Fixed-Bed Adsorbers and Reactors

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Both analytical and numerical solutions are derived to quantify thermal and radial effects in non-isothermal fixed-bed adsorbers and reactors. Unavoidable temperature fluctuations are frequently typically neglected. One goal of our study is to quantify how temperature gradients can influence retention, resolution and conversion of reactants into products in fixed-bed adsorbers and reactors for smaller deviations from isothermal behavior. In contrast to the previous studies [1-4], another goal of this work is to include the possibility that radial concentration profiles can develop [5]. For that purpose, a two-dimensional fixed-bed model is formulated in cylindrical geometry. The model equations form systems of convection-diffusion type partial differential equations coupled with algebraic equations describing thermodynamic and kinetic phenomena. The coupling of concentration and thermal fronts is illustrated and key parameters characterizing the impact on fixed-bed performance are evaluated for typical thermodynamic and kinetic parameters and process conditions. In many chromatographic operations, injected sample volumes are small and the feed solutions are diluted. Therefore, the assumption of linear adsorption isotherm is often valid. The Laplace and Hankel transformations are jointly applied to derive analytical solutions of the linear model equations. The numerical Laplace inversion formula is employed to get back solutions in the actual time domain. To further analyze the effects of different kinetic parameters on the elution profiles, statistical temporal moments for both the concentration and temperature profiles are derived. In the case of nonlinear adsorption isotherms, a high resolution flux limiting finite volume scheme is applied to solve the model equations numerically. Several case studies are carried out to analyze the effect of different kinetic and thermodynamic parameters on the effluent concentration profiles. The developed analytical and numerical solutions could be useful for the estimation of model parameters from results of laboratory-scale experiments and for improving the process by suppressing or maximizing the thermal and radial effects.

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# UNRAVELLING ELECTROCHEMICAL LIGNIN DEPOLYMERIZATION: KINETICS MODELLING USING POPULATION BALANCE EQUATIONS

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In the presence of climate change evidence, renewable energy and resources have become vital elements for a future sustainable chemical industry. [1] Lignin valorisation via electrochemical depolymerization is a promising approach for commercial application due to its moderate reaction conditions. [2] However, there is no available kinetics model for this reaction. Conventional reaction kinetics equations are inadequate when used for lignin degradation because of the limited kinetics information with respect the reaction mechanism. We suggest to use population balance equations to predict the evolution of molecular weight distribution (MWD) of lignin with time.

A polymer can be decomposed by random and/or chain-end scissions. The general reaction schemes are as follows:

Random degradation: $\boldsymbol{A(x') \rightarrow A(x) + A(x' - x)}$

Chain-end degradation: $\boldsymbol{A(x') \rightarrow A(x_i) + A(x' - x_i)}$

where $x_i$ is the molecular weight of the specific unit $A(x_i)$ (monomer) that is detached from a polymer $A(x')$ with molecular weight (MW) of $x'$. The rate coefficient for degradation of $A(x')$ is $k(x')$. $A(x)$ is a random polymer that is cleaved from $A(x')$ and has $x$ molecular weight.

In population balance, the time dependent MWD is denoted by $p(x,t)$. For MW range of $x$ to $x + dx$, the random depolymerization rate can be written as follow:

$$dp(x,t)/dt = -k(x)p(x,t) + 2\int_x^\infty k(x')\,p(x',t)v(x,x')dx'$$

where, $v(x,x')$ is the fraction of $A(x')$ that cracks to $A(x)$. [3] Similar population balance equation can describe also the chain-end scission. The depolymerized products of lignin are categorized based on their degree of polymerization (DP) where DP1 is the monomer with a suggested molecular weight of 210 g mol$^{-1}$.

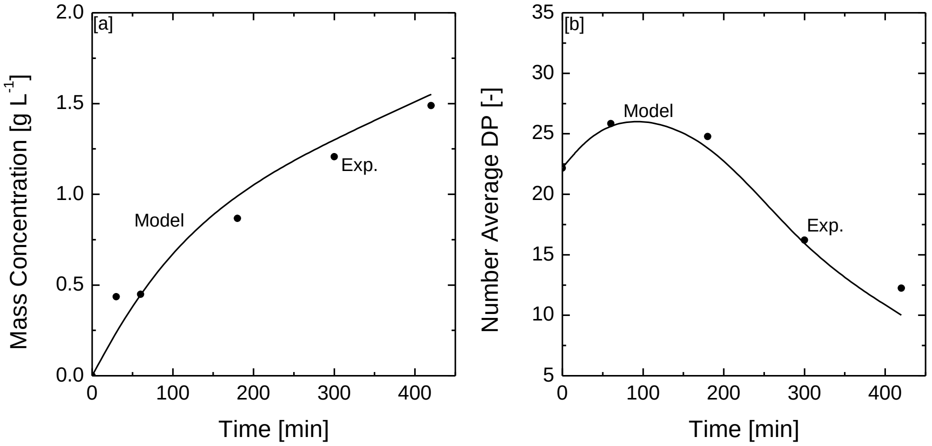

Figure 1: Experiment and model results for the product formation [a] and the number average DP [b].

Solving the low MW population balance equations, using fixed pivot technique, is carried out discretely whereas a continuous solution was implemented for the high MW, up to 3 Mg mol$^{-1}$. [4] Additionally, the model accounts for a recombination reaction of the depolymerized species. The model is capable of predicting the MWD of lignin as a function of electrochemical processing time. New experimental results are used to extract reaction constants for different kraft lignin samples. The reaction constants were determined using “nonlinear least-squares curve-fitting” in MATLAB. Figure 1a shows the product (monomer) formation and Figure 1b displays the prediction of the number average DP for the depolymerized lignin with time.

The kinetics model is used to develop an electrochemical membrane reactor scheme in gPROMS to optimize the electro-oxidation of lignin. As a result, the effect of the over-oxidation towards the desired products can be minimized.

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# Geometrical optimization of steam cracking coils

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The cracking process converts heavier, less valuable fractions of crude into lighter products such as olefins. To maximize the olefin yields, it must usually be performed at high temperature and low pressure, heat being required to break the heavier elements into lighter ones. The temperature distribution in the reactor is a key parameter of steam cracking, as a too high temperature on the inner surface of the reactor leads to coke formation, which is damageable to the process on the long term because of reduction of the heat transfer efficiency. Artificially increasing the roughness of the inner surface of the reactor is a passive and efficient method to enhance turbulence and heat transfer, leading to a more homogeneous temperature distribution inside the coil, as represented in Figure 1. This method however induces an increase in pressure loss, i.e. an increase of injection pressure, which is detrimental to the olefin production process and must be limited.

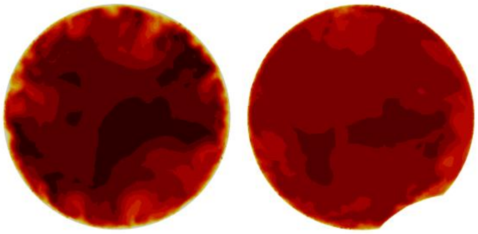

Figure 1: Temperature distribution in a smooth reactor (left) and a ribbed reactor (right).

Numerical simulation of steam cracking is still extremely challenging because of the size of the computational domain, the complex flow dynamics and the stiffness of the chemical mechanism. It requires accurate unsteady approaches to describe the turbulent reacting flow, such as Large Eddy Simulation (LES). Due to the computational cost of LES, a methodology was developed and applied to the steam cracking flow in ribbed coils with a reasonable computing time. It uses a periodic configuration, the correct flow dynamics and thermochemistry being ensured by specific source terms added to the conservation equations. This methodology was implemented in the AVBP code of CERFACS which solves the compressible reactive

Navier-Stokes equations using the LES approach, and was validated against detailed experimental measurements.

In this work, the optimization of the internal reactor coil geometry is performed based on Gaussian processes [1] and series of LES to maximize the ethylene production. The study focuses on helically ribbed cracking coils, the size and pitch of the rib being two parameters to optimize. The possibility to include rib discontinuities of various size, as illustrated in Figure 2, is also investigated, leading to a total of four geometrical parameters to optimize. The optimization software BATMAN [2] developed at CERFACS is used for a completely automatic optimization procedure, including statistical prediction of the response surface thanks to Gaussian process and progressive addition of new simulations with the expected improvement method [3]. An analytically reduced cracking mechanism [4] is included to the simulations to predict the chemical composition at the reactor outlet, and a coking model [5] is used to estimate the coke formation rate at every location in the reactor. The optimization algorithm focuses on the products mass flow rate at the outlet and the run length of the process to maximize the ethylene production over time. This work leads to a new geometry of the cracking coils which maximizes the ethylene production thanks to an optimal temperature distribution and limitation of the pressure losses.

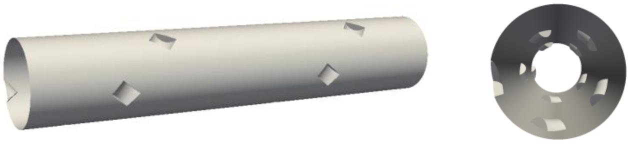

Figure 2: Example of discontinuously ribbed reactor geometry.

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# Adaptive reaction network size control for the catalytic conversion of renewable resources

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Reaction network generation and analysis, including a microkinetic assessment of the catalytic conversion of renewable resources, represents a key challenge for a sustainable future [1]. Due to their complexity, such networks are preferably handled by an automized method, e.g., via an incremental procedure to determine all possible products from initial reactants via selected reaction families. To prevent the infinite generation of new elementary steps and corresponding species and to ensure that the reaction network focuses on the most relevant steps and species, adequate decision criteria are required to determine which ones should be minimally accounted for.

State-of-the art network generators control the extent of the reaction network in two ways, either by reducing the model *a priori*, i.e., while generating the reaction network or *a posteriori*, i.e., after having generated the full reaction network [2, 3]. A distinction can also be made between rule-based size control, relying on rules reflecting the chemical expertise of the modeler, and rate-based size control, only including the kinetically significant reactions in the model. By applying rule- and rate-based criteria, state-of-the-art network generation results in a single static network, in which no variations as a function of operating conditions are taken into account.

Answering the need identified above, we here propose a methodology for adaptive reaction network size control. It exhibits a unique and previously non-existing feature, i.e., the ability to extend or reduce the reaction network in an adaptive manner as a function of the space time or clock time, depending on the reactor type, without requiring the intervention of the modeler. The most significant benefits of the methdology, as well as the most severe challenges are situated in the most extended reaction networks. Constraining the networks to the most relevant steps, in an adaptive manner, results in an overall tangible simulation time, yet the evaluation of course also takes time. An optimal balance should be pursued between the simulation time and the time consumed for identifying the relevant steps and species in the network.

The construction of the application is based on three stages of development, see Figure 1. In each stage, more intelligent criteria are applied for network size control, starting from a simple rate of production analysis performed at regular intervals towards a criterion-based selection of the relevant zones within the reactor, i.e., where the reaction network reduces or extends. The criterion, which is still being worked on, takes both the historic and the pointwise importance of the species into account and serves as a less expensive, preliminary assessment before applying a rate of production analysis.

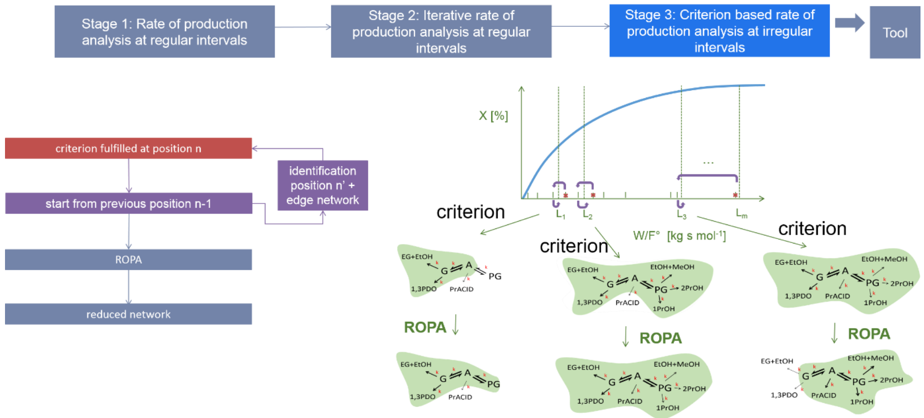

Figure 1. Overview of the three development stages of the tool for adaptive size control, with a focus on the third stage 'criterion based rate of production analysis', and applied to the hydrogenolysis of glycerol

Glycerol hydrogenolysis in a plug flow reactor serves as the test case for the developed network generation methodology. Since glycerol hydrogenolysis can be described by a relatively simple reaction network, for which the manual construction is still feasible, it serves as a good proof-of-concept and a solid base for the future automized assessment of more complex networks [4].

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## Acknowledgements

This work was supported by a doctoral fellowship from the Fund of Scientific Research Flanders (FWO), the European Research Council under the European Union's Seventh Framework Programme (FP/2014-2019) / ERS grant agreement n° 615456 and the 'Long Term Structural Methusalem Funding by the Flemish Government'.

# Biomass Hydrodeoxygenation: A Combined Experimental, First-Principles and Mathematical Modelling Study

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Recently, a considerable effort has been devoted to substituting the petroleum-based chemicals with the biomass-based chemicals. Biomass consists of three main polymer units: lignin, cellulose and hemicellulose, together covering a large spectre of all possible biobased chemicals. We focus primarily on the industrially important chemicals, chiefly on the lignin-derived aromatic compounds, the cellulose-derived (di)carboxylic acids and (poly)alcohols, and the furan-ring-containing chemicals from hemicellulose.

In our work, we combine experimental work with mathematical modelling and theoretical calculations. The experiments were carried out in a three-phase slurry reactor, in which the model compounds for each biobased unit were dissolved in a liquid solvent. In the gaseous phase, hydrogen at high pressure is present and a solid catalyst is added to the reaction mixture. The liquid and gaseous phases are regularly sampled and analysed using the gas chromatography (GC, GC-MS) and/or liquid chromatography (HPLC).

As the model compound for lignin, eugenol was used.[1] Different linear alcohols, acids, ketones, aldehydes, ethers and esters with the chain length of 6 carbon atoms presented the model compounds for cellulose.[2] To model hemicellulose, levulinic acid was chosen.[3] The aim of our work was to establish a mechanistic microkinetic model for a three-phase slurry reactor. As an additional input, quantum chemical calculations were performed to elucidate the details of the mechanism of the biomass hydrodeoxygenation (HDO).

The mathematical model included mass transfer of hydrogen and compounds from the gaseous to the bulk liquid phase, where the intrinsic concentration of $H_2$ on the liquid side of the gas–liquid interphase is evaluated with Henry's law. Mass transfer of $H_2$ and the model compounds from the liquid phase to the catalyst surface and their adsorption/desorption kinetics are also defined. Lastly, chemical reactions on the catalyst surface, which are generally the dominant chemical transformations, and chemical reactions in the bulk liquid phase are taken into account. All reaction rate constants are considered temperature-dependent according to the Arrhenius law.

Furthermore, the molar balance of hydrogen and each model compound in all relevant phases is described with differential equations within the mathematical model. The proposed set of differential equations is solved using the Matlab software. The experimental data are compared with the model results using the least squares approximation method.

For additional verification of the phenomenological mathematical model, several *ab initio* calculations were performed using the density functional theory (DFT). Modelling the catalyst as a slab of crystalline $MoS_2$ with some substituted Ni atoms in the top layer, adsorption energies of the relevant six-carbon acid, ketones, aldehydes and alcohols were calculated. Assuming that hydrogen dissociatively adsorbs to the Ni and S sites, the activation barriers for the transformation of the aforementioned species were calculated. The results were consistent with the solutions of differential equations based on the experimental results. We thus believe that the model is sound.

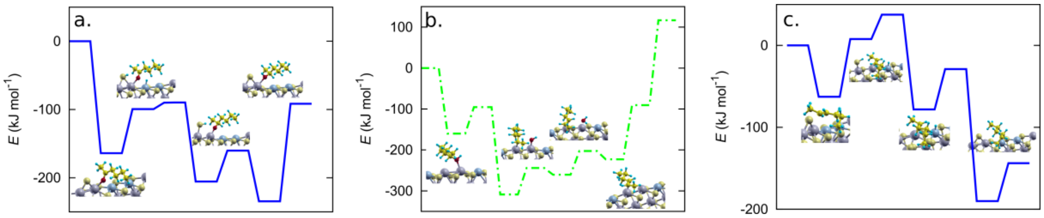

**Figure 1**: The potential energy landscape of ketone hydrogenation to alcohol (a), alcohol dehydration to alkene (b), and alkene hydrogenation to alkane (c).

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# ON THE REACTIVITY OF MONO-LIGNOL DERIVATIVES

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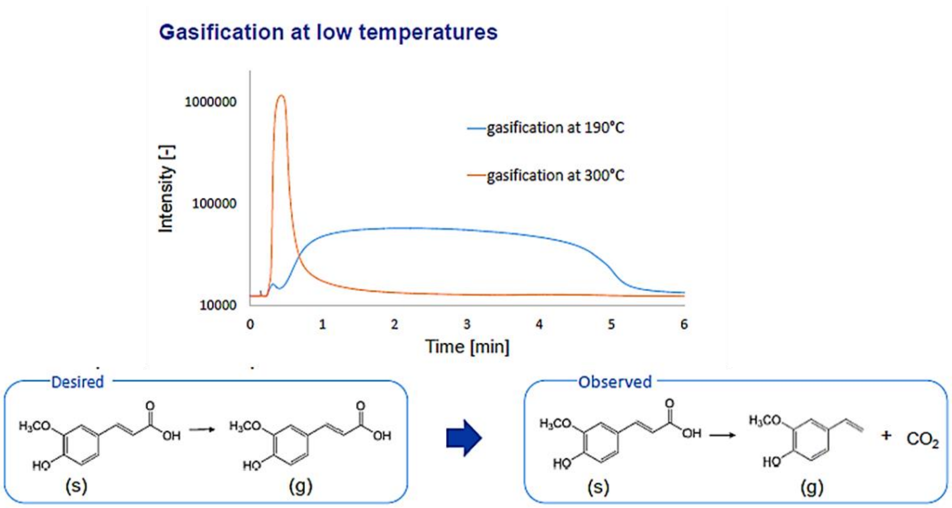
The valorization of lignin, the second most abundant component of lignocellulosic biomass, has remained a challenge for many years. Given the large concentration of phenolic groups, lignin appears to be a good potential candidate for the production of aromatic chemicals such as catechols and p-vinyl phenols. Production of such chemicals requires the ability to depolymerize lignin in a controlled manner. The thermochemical route uses fast pyrolysis to crack lignin polymers to smaller fragments. In order to be able to do so in a guided way, the thermal decomposition chemistry of lignin needs to be understood in great detail.

Lignin is mainly built from three monolignols, which are derivatives of cinnamyl alcohol and distinguish themselves through the aromatic unit, viz. p-hydroxy phenyl (H), guaiacyl (G), and syringol (S). Lignols are connected via β-O-4, α-O-4 ether and 8-8 linkages. It is assumed that both, the substitution pattern of the benzene ring and the linkage between the units have strong impacts on the product distribution. Efforts are underway to generate kinetic models able to describe these impacts and to predict pyrolysis product spectra as a function of operation condition. So far, the pyrolysis studies coupled with EPR analysis of monolignols and their derivatives provide mechanistic information of their thermal decomposition. However, very few studies focus on the intrinsic pyrolysis kinetics of these lignin model compounds.

The current work presents a comprehensive study of the fast pyrolysis kinetics of lignin model compounds such as cinnamic acid, p-coumaric acid, ferulic acid and their derivatives phenol, guaiacol and syringol. This study is performed with a two-stage micropyrolyzer setup connected on-line to the injector port of the GC. The setup also consists of an external 6-port valve to introduce a pulse of internal standard gas (neon-butane mixture) to allow easy quantification of the products. The GC x GC-FID/MS is equipped with a cold-trap cooled cryogenically for the entire duration of the reaction to refocus the product molecules. The molecules are then released based on their boiling points during the cold-trap heating. The light molecules are analyzed using a special GC with TCD and PDD detectors.

All the experimental conditions are designed in such a way that the transport effects are faster than the reaction kinetics. Sample sizes of 50-100 µg have been used in order to avoid possible mass transfer effects. In this work, one set of experiments provide intrinsic kinetics of solid-to-gas transformation of lignin model compounds obtained by connecting the 1st reactor directly to the GC x GC-MS/FID. The samples are assumed to be instantaneously heated while being dropped into the first-stage heated reactor eliminating the effects of heating rates on the product evolution.



In the second type of experiments, the first stage of the micropyrolyzer is used for vaporization of the samples and the second stage acts as an isothermal plug flow reactor, which can be operated up to 900 ˚C. The preliminary results show that the acids of monolignols decompose into their vinyl counterparts and $CO_2$ at temperatures as low as 160-190 ˚C. The gas-phase pyrolysis product profiles thus obtained will be interpreted with mechanistic information found in the literature and utilized in the future to construct a detailed kinetic model for lignin decomposition.

### Acknowledgements

**This work is supported by the 'Long Term Structural Methusalem Funding by the Flemish Government'. The SBO proposal "Bioleum" supported by the Institute for promotion of Innovation through Science and Technology in Flanders (IWT) is also acknowledged.**

# TITANIUM BASED COMPOSITE SYNTHESIS AT THE CONDITIONS OF CONTROLLED HEATING

1

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Titanium based composites are interested for numerous applications. Nowadays similar composites find a use in additive manufacturing including electron beam and laser melting. The synhtesis of composites on the sybstrate directly from initial powders of pure substances (titanium, aluminum, carbon, boron, and etc.) meets the difficulties connecting with different properties of substances, that does the process uncontrollable. Hence the composite powders are more suitable for practical applications. The synhtesis of such composites can be carried out based on SHS-methods. The volume synthesis or the synthesis in the explosion mode has some preference in comparison with the mode of layerwise combustion, since there is the most homogenization of synthesized product in a first situation and it is possible to control the process by means of the change in the thermal contact conditions of the reacting system with the environment and with the heater. This process can be controllable when the initial mixture composition is varied, inert particles are used as admixtures; the heating rate and the heating way are changed; external mechanical loading could be applied.

In the case of thermal explosion mode, the reactions happen in the volume homogeneously or not very homogeneously and are accompanied by high heat release that decreases due to inert admixtures or due to non-stoichiometric initial composition. The final composition of the synthesis product turns out irreversible and depends on numerous factors. The reagent dispersion, admixture presence, initial porosity, heating way, pressing size and geometry, and etc. belong to important factors. In the simplest models of controlled thermal explosion [1, 2], the chemical process is described by summary reaction scheme. This is due to pure understanding of mechanism of chemical reactions in solid phase. The known concept of reaction cell is developed for ideal systems corresponding to quasi stationary conditions, weakly suitable for real situation. The conditions of dynamical thermal explosion can be realized for numerous systems [3, 4].

In this paper the models with detailed reaction schemes are suggested for the systems (Ti-Al) + C (B, Si). Thermodynamics is used to evaluate the formal kinetic parameters; however the activation energies are corrected because solid-phase diffusion is limiting stage in this case. This leads to use special kinetic functions taking into account reaction retardation by solid product. The model is modified for different variants of the reactor. Taking into account the temperature distribution along thickness of the powder compact allows analyzing the role of not uniform heating or not uniforming initial composition in the dynamics of the synthesis. However non stoichiometric composition dos not guarantee the explosion mode for the synthesis.

The numerical realization of the model is carried out using different methods including non-explicit Euler method, some variant of Runge-Kutta method, and etc. The features of kinetic equation systems are studied also separately at the conditions of given temperature evolution. When temperature distribution along solid-phase reactor is taken into consideration, the non-explicit difference scheme and double-sweep method are used.

The models of controlled thermal explosion and volume sintering of composites are verified with the help of experimental data for corresponding conditions.

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# INVERSE HYSTERESIS IN THE CO OXIDATION OVER PALLADIUM: INFLUENCE OF THE CONVECTION ON THE DYNAMICS

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Under TPR studies of CO oxidation on the Pd foil in the flow reactor, we observed the inverse hysteresis in dependence of CO conversion on the temperature. The XPS studies demonstrated that under heating the metallic palladium on the foil surface oxidized to the surface oxide (2D-PdO). At high temeperatures, the 3D-PdO clusters were observed. Under cooling the subsequent reduction of the palladium oxide proceeded and the self-oscillations of CO conversion caused by the oxidation-reduction of the palladium surface were also observed.

To describe the experimental data we have proposed the mechanism of the reaction as well as the lumped mathematical model, which describe to the dynamics of the reaction in the CSTR reactor. Moreover, to describe the reverse hysteresis, we used the previously developed stepwise appoach [1,2], i.e. we considered the nonlinear dependence of the energy of activation of a certain elementary step of the reaction on the fraction of 3D-PdO on the palladium surface. However, the proposed model has predicted the U-shape dependence of the CO conversion on the temeprature, which was not existed in the experimental data. The model has predicted such a dependence under cooling due to reduction of less active 3D-PdO and fromation of more active 2D-PdO.

In this work, we have studied the model, which describes the dynamics of the reaction in a flow reactor with some equal layers in flow direction and the whole volume of reactor equals to the considered volume of the CSTR reactor. As a limit case we considered the corresponding model of the plug flow reactor.

Using both the qualitative methods of dynamical systems and simulations, we have qualitatively described the experimentally observed inverse hysteresis (Fig.1a). In this case, there is no U-shape dependence under cooling.

We have studied the dynamics of the reaction depending on the number of layers along the flow direction. In particular, we have found the conditions under which the dynamics changes from the steady state to regular oscillations and then to chaotic oscillations along the reactor axis. The chaotic oscillations in some layers are caused by the convection process and can be considered as forced oscillations, i.e. interaction of the self-oscillations and oscillations from the previous layer.

Moreover, under self-oscillations conditions the model has predicted the front of the degree of oxidation of the palladium surface moving in direction to inlet of the reactor (Fig. 1b).

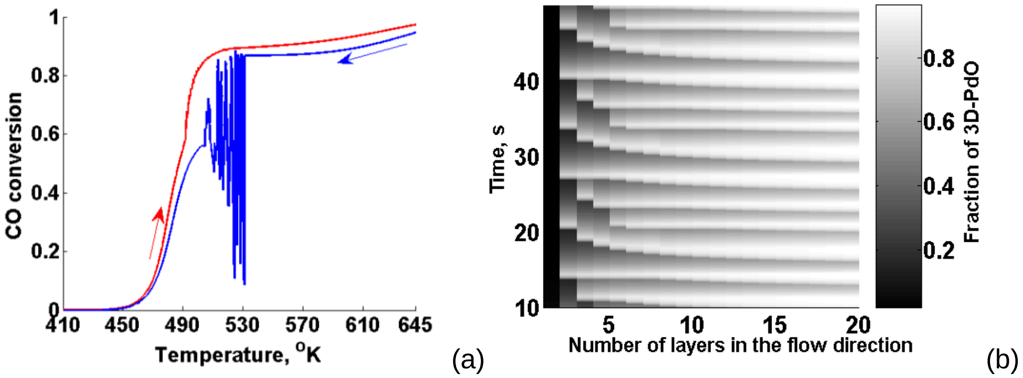

**Fig. 1**. (a) The inverse hysteresis dependence of CO oxidation on the temeprature. (b) Dependence of the fraction of 3D-PdO on the surface of palladium foil over time and the length of the flow reactor.

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# Catalyst ignition in a gas-solid vortex reactor for oxidative coupling of methane: a numerical study

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The decreasing crude oil reserves and the increased availability of methane from shale gas and stranded gas reserves have created a strong economic interest in developing processes that allow methane conversion into more valuable products. One of the most promising routes to directly convert methane into ethylene and higher hydrocarbons is the oxidative coupling of methane (OCM). Ever since the pioneering work of Keller and Bhasin [1], OCM has attracted both industrial as well as academic interest. Studies available in literature have focused on the optimization of catalyst composition, reactor design and operating conditions in order to increase the methane conversion and C2 selectivity. However, the reported C2 yields are generally very low, with the upper limit currently at 26 % [2]. One of the reasons for the low C2 yields is the low methane conversion that is required to avoid runaway of the highly exothermic process. Depending on the methane-to-oxygen ratio in the feed, adiabatic temperature rises from 300 to 1500 K have been reported, which indicates the importance of a good heat management system [3]. A full understanding of the ignition and extinction behavior is thus a requirement for designing a new OCM reactor and associated temperature control system.

In this work, we first present a bifurcation analysis of methane oxidative coupling using detailed gas phase and catalytic kinetic mechanisms at broad ranges of reactant ratios, pressure, inlet temperatures and reactor configurations. A comparison between three ideal adiabatic reactor models is made: plug flow reactor (PFR), continuously stirred tank reactor (CSTR) and lumped thermal reactor (LTR), the latter representing the limiting case with zero backmixing (cfr. PFR behavior) for species and perfect thermal backmixing (cfr. CSTR behavior). In both the CSTR and LTR, thermal backmixing is responsible for steady state multiplicity. Among the three investigated reactor types, a LTR shows the highest product yields and the lowest extinction temperatures, which allows autothermal operation at a much lower inlet temperature compared to a PFR and CSTR. The LTR is therefore selected as the preferred reactor configuration for OCM.

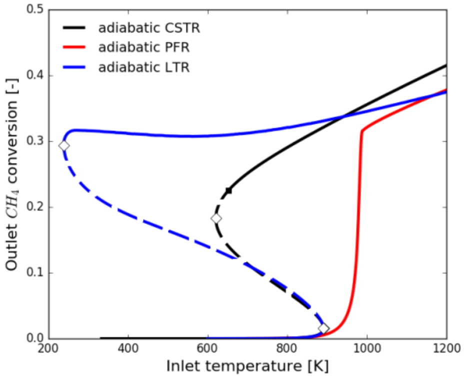

*Figure 1: Comparison of adiabatic PFR, CSTR and LTR for OCM with Sn-Li/MgO catalyst: methane conversion as a function of inlet temperature. Operating conditions: P = 1 bar, $CH_4$:$O_2$ = 6, $V/F_{CH4,0}$ = 0.02 s, $m_{cat}/V$ = 1000 $kg_{cat}/m^3$. (■: Hopf bifurcation, ◇: fold)*

The remaining question is related to the practical aspects of realizing such a reactor with minimal species backmixing and maximal thermal backmixing. We propose the gas-solid vortex reactor (GSVR) [4] as the reactor type most closely resembling the LTR. Computational Fluid Dynamic (CFD) simulations have shown that the residence time distribution of inert species in a GSVR shows a lot of plug flow behavior, indicating limited species backmixing. Meanwhile, temperature profiles inside the catalyst bed are quasi-uniform, corresponding to the hypothesis of perfect thermal backmixing.
Extending on the results obtained with the bifurcation analysis, CFD simulations will be used to show that it is possible to operate the GSVR autothermally on the ignited branch, leading to C2 yields of ~20%.

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# Non-linear waves and cardiac arrhythmias

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Cardiac arrhythmias and sudden cardiac death are the leading causes of death, accounting for about 1 death in 10 in industrialized countries. Although cardiac arrhythmias have been studied for well over a century, their underlying mechanisms remain largely unknown. One of the main problems in studies of cardiac arrhythmias is that they occur at the level of the whole organ only, while in most of the cases only single cell experiments can be performed. Due to these limitations, alternative approaches such as mathematical modeling are of great interest. From a mathematical point of view, the excitation of the heart is described by a system of non-linear parabolic PDEs of reaction-diffusion type with anisotropic diffusion operator. Cardiac arrhythmias correspond to the solutions of these equations in the form of 2D or 3D vortices characterized by their filaments.

In my talk I will present a basic introduction to cardiac modeling and mechanisms of cardiac arrhythmias and briefly report on main directions of research on this topic in the world and at Ghent University's clinical and basic science departments. I will also provide example of our research on the development of a virtual human heart model and its application to study mechanisms of arrhythmias due to dynamical instabilities in cardiac tissue, fibrosis and heterogeneity.

For my papers please visit
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# A Cybernetic Approach to Modeling Lipid Metabolism in Mammalian Cells

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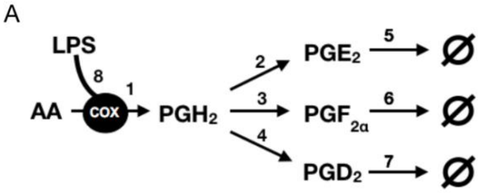
Metabolism is regulated by a number of factors in the cell. The concerted action of metabolism and regulation gives rise to the cellular phenotype or cellular outcome behavior. The cybernetic approach developed by our group builds on the perspective that metabolic regulation is organized towards achieving goals relevant to an organism's survival or performing specific biological functions. The key advantage of cybernetic descriptions of cellular regulation is that they capture the molecular phenomena that control metabolic fluxes. Regulatory goals, such as maximizing growth [1] or carbon uptake rate [2], provide a causality driven basis for the regulation of individual chemical events.

While cybernetic models have focused on bacterial systems in the past, we presently adapt this framework to model the dynamic behavior of prostaglandin (PG) formation in a mammalian cell line. PGs are a well characterized set of inflammatory lipids derived from arachidonic acid (AA). They are widely studied due to their influence on inflammation and related functions. Several kinetic descriptions of PG formation precede this work [3, 4], but none take into account the regulatory phenomena present in PG formation. Our application of cybernetics to macrophages provides a quantitative model of eicosanoid metabolism initiated with the input of AA and resulting in the inflammatory outcome represented by TNF-alpha.

To describe the time-dependent formation of PGs, a cybernetic model is generated. This description approximates the conversion of AA into downstream products (figure 1A).
In using cybernetic arguments to model PG formation (figure 1B), we are assuming that these products are formed in varying amounts related to their ability to help the cell achieve its inflammatory objective. The production of PGs that have a stronger

relationship with the goal of the system will be upregulated while the pathways for those PGs which have a lesser relationship with the objective function will be downregulated.



B

$$\frac{dPGH_2}{dt} = r_{AA\rightarrow PGH_2} - \sum_{i=1} v_i e_i r_{PGH_2\rightarrow PG_i}$$

$$\frac{dPG_i}{dt} = v_i e_i r_{PGH_2\rightarrow PG_i} - r_{PG_i\rightarrow \emptyset}$$

$$\frac{de_i}{dt} = \alpha_i + u_i \frac{k_{E,i} PGH_2}{K_{E,i} + PGH_2} - \beta_i e_i$$

Figure 1: A) Network for the metabolism and signaling pathway of lipopolysaccharide (LPS) stimulation that leads to the catalysis of PGs from AA via the enzyme COX (cyclooxygenase). B) In addition to changes in metabolites, the relative changes in enzyme level $e_i$ (modeled as a function of constitutive formation, induced formation, and degradation) for each pathway are also modeled with ordinary differential equations. Regulation is implemented via $u$ and $v$, the cybernetic control variables. The dynamic variable $u_i$ represents the regulation of induced enzyme formation, and $v_i$ modulates enzyme activity which typically occur through allosteric mechanisms.

After fitting parameters to two conditions (i.e., the control and KLA treatment conditions), it is evident that the model correctly explains the evolution of the metabolite concentrations involved in the fit. The kinetics of the model are cross-validated using additional treatment conditions. Cybernetic models are a robust description of metabolite formation and can be used to predict perturbations to metabolism via various effectors including drugs. This work, for the first time, develops the idea that cybernetic metabolic objectives can be used to describe the regulation of signaling systems in mammalian metabolism. It yielded a model describing PG synthesis that is capable of predicting metabolite levels, as well as, provide robust predictions of how drugs that inhibit $PGH_2$ formation alter the downstream generation of PGs for pursuits in translational research.

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# Chemical kinetics of brain metabolism: Equilibrations and Control of the process

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The role of lactate in the brain as a fuel and signalling molecule in neuronal activity, is considered important especially during neuronal activation. The metabolic coupling of neurons and astrocytes establishes the Astrocyte to Neuron Lactate Shuttle (ANLS), in which astrocytes provide lactate to neurons. The mathematical models governing the processes of brain metabolism are multi-scale in character, due to the wide range of time scales characterizing the various sub-processes. In such multi-scale models, it is often challenging to identify the important processes and the characteristic time-scales of the system. Here, we provide unique insights utilizing the Simpson et al. model [1], after proper parameter fitting, in order to reproduce human data [2].

The complex brain lactate kinetic model is analysed using the Computational Singular Perturbation (CSP) algorithm [3]. Our goal is to provide the underlying physical understanding of the various features exhibited in brain metabolism. CSP is used here to identify (i) the processes generating the fast and slow time scales, (ii) the processes contributing to the established equilibrium states and (iii) the processes that control the evolution of the chemical species. CSP tools identified eight equilibrium states, four that refer to the Glucose pathway and four that refer to the Lactate pathway, as displayed in Figs. 1 and 2. The system evolves within the confines imposed by these equilibria and is driven by slow components of the model that can identified by CSP. These are components that influence (i) the duration of the neuronal activation time and (ii) the desired levels of targeted metabolites, so they are able to manipulate neuronal activation.

This new algorithmic approach of asymptotic analysis is not hindered by the complexity or the size of the brain metabolism kinetic mechanism and yet provides useful insights regarding the underlying physics. We demonstrate these capabilities by validating the metabolic profiles of neurons and astrocytes and by providing further computational proof of the well supported experimentally ANLS hypothesis. We further investigate the response of the system under exercise conditions, in order to demonstrate the ability to examine such conditions of brain metabolism or more complicated like brain disorders and drug therapy.

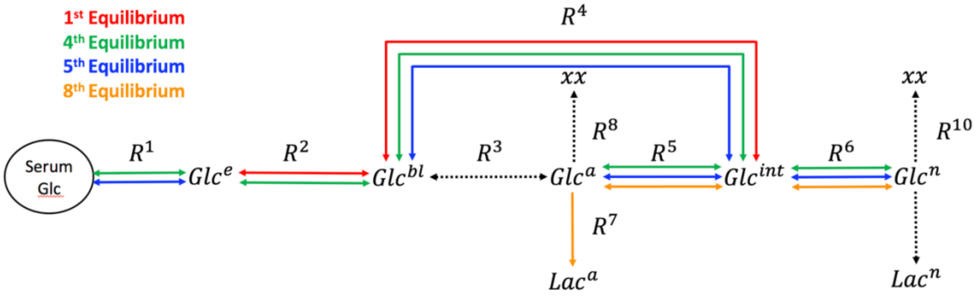

Figure 1: The Glucose pathway defined by 4 equilibrium states.

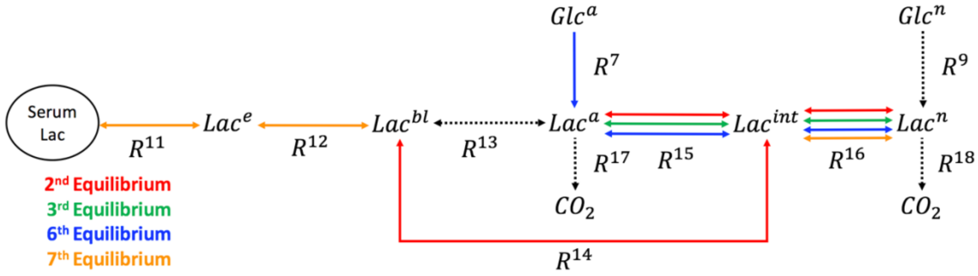

Figure 2: The Lactate pathway defined by 4 equilibrium states.

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# TRANSIENT KINETIC ANALYSIS OF MULTIPATH REACTIONS USING STEP-RESPONSE AND TAP METHODS

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Catalytic reactions frequently proceed through multiple paths due to existence of various active sites on the catalyst surface. Transient methods were developed to complement the steady-state kinetic analysis and to provide additional information to discriminate reaction paths and to estimate the kinetics of elementary steps. The step-response and temporal analysis of product (TAP) methods are widely used transient methods.

The utilization of computer-aided educational modules in the undergraduate and graduate curriculum was proven to have a positive impact on the chemical engineering pedagogical field. The recently developed IPython notebook system allows to mix the model explanation, run a computer code, and visualize simulation results in a single web-based environment.

This paper presents the computer-aided educational modules to learn the application of step-response and TAP transient methods to kinetic analysis of multipath reactions. The oxidation of carbon monoxide was chosen as an example of multipath reaction due to its simplicity, diversity of transient behavior and industrial importance. The carbon monoxide oxidation on zinc catalyst (Kadox 25, New Jersey Zinc Co.) proceeds through the reaction between adsorbed carbon monoxide and adsorbed neutral oxygen species according to the Langmuir-Hinshelwood (LH) mechanism, and the reaction between gaseous carbon monoxide and ionized oxygen species following the Eley-Rideal (ER) mechanism [1].

The step-response method consists of the analysis of transient responses of the product concentration at the fixed-bed reactor outlet on the step change in the concentration of reactant at the reactor inlet. The IPython educational module was developed to simulate numerically the unsteady-state mass balance equations for the gas-phase components in the fixed-bed reactor and mass balances for surface intermediates on the catalyst active sites [2]. The typical response curves to the step-changes in inlet concentration (Fig. 1a) are shown in Fig. 1b.

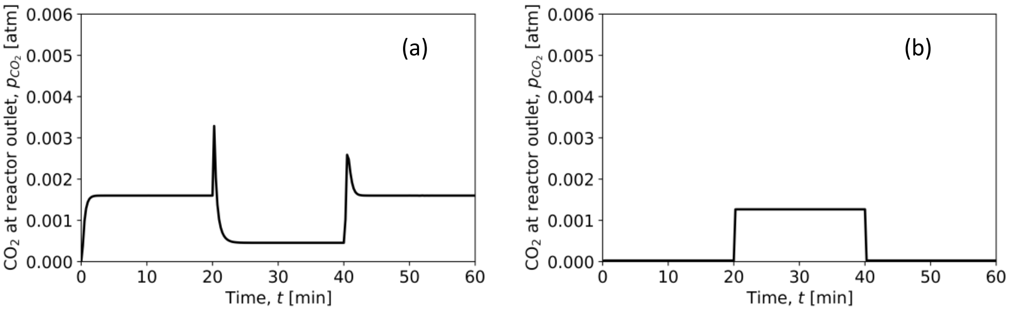

Fig.1 Transient responses of step-response method: (a) LH route, (b) ER route.

The TAP method is based on the analysis of reactant and product concentration at the outlet of the catalytic microreactor operating under vacuum to the pulse input of reactant at the reactor inlet. The IPython module was developed to solve numerically the system of PDE-ODE mass balance equations. The typical transient responses of the TAP method are shown in Fig. 2. Our simulations confirm that the rate of carbon dioxide formation decreases with temperature for both LH and ER routes, whereas the exit flow rate of $O_2$ increases with temperature in the LH route and does not change significantly in the ER route.

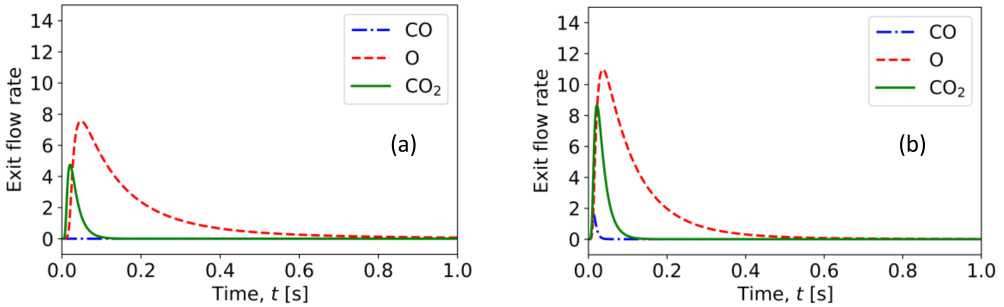

Fig.2 Transient responses of TAP method: (a) LH route, (b) ER route.

The developed computer-aided educational packages can help students to acquire both theoretical and practical skills related to the kinetic analysis of complex reactions. The researchers can easily modify the computer packages and use them for the analysis of various reactions.

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# MATHEMATICAL MODELLING FOR BIMODAL CATALYST DEACTIVATION

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Finding the optimal textural and geometrical characteristics for the catalysts with hierarchical system of pores is one of the crucial problems for heavy oil refining industry [1]. Theoretical modelling of media with complicated texture and processes of medias evolution should make this search much easier.

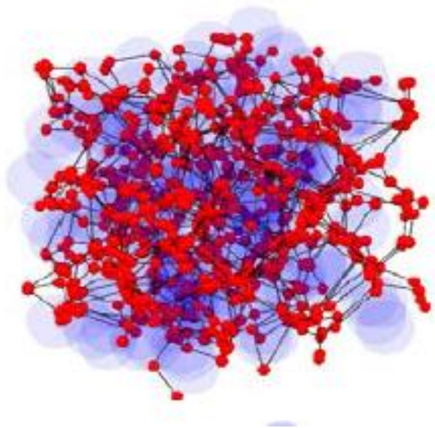
We model the body of alumina as a unit of fully penetrated spherical granes in a cube $\mathbf{K}$ with constant radii and Poisson distributed coordinates of the centers. The deactivation process is simulated as the uniform growth of granes radii. The geometrical characteristics of the porous space – porosity $\varepsilon$, specific surface area $S$ and tortuosity $\tau = \frac{L_{pore}}{L_{Eucl}}$ – change greatly. From the dependence $\Psi^2 = \frac{\tau}{\varepsilon} \cdot S \cdot \frac{K}{D_{bulk}}$ between geometrical and chemical charteristics of the catalytic media and reagents it is possible to calculate the effectiveness factor $\eta = \frac{\int Kc}{Kc_0}$ of the catalyst. Here the concentration of the asphaltenes $c=c(\xi,z)$ is the function of two variables $\xi$ – radius of the cylidrical pellet and $z$ – height of the pellet, integral is taken by the cylinder. It is calculated at every stage of deactivation from the Fick's law which under the assumption of stationarity is turned into elliptic equation on $c(\xi,z)$

$$\frac{d^2c}{d\,\xi^2} + \frac{d^2c}{d\,z^2} + \frac{1}{\xi} \cdot \frac{d\,c}{d\,\xi} = \Psi^2 \cdot c \qquad (1)$$

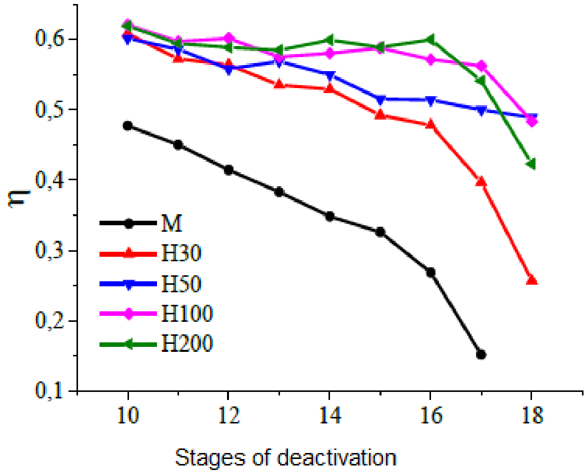
The stationarity means that the deactivation process passes with such a slow rate that the distribution of the contration in the pellet satisfy timeless equation (1). Equation (1) can easely be solved by common mathematical packets.

The main difficult in that approach was to calculate tortuosity of reducing porous space. The system of pores was approximated by the percolation graph obtained from the Voronoi diagram of the Delaunay decomposition, centers of the pores correspond to vertices of the graph and canals between pores correspond to the edges. During the deactivation percolation graph loses its vertices and edges as pores and canals become carbonized. Tortuosity of the sample icreases as the legth $L_{pore}$ of path from one facet of **K** to the opposite facet become longer. The specific surface area $S$ and porosity $\varepsilon$ are calculated from the standard Monte-Carlo methods [2].

Template method can produce macropores inside the catalytic media with diameter from 50nm to 200nm. To simulate macropores in the according domains in **K** spheres that modeled granes were simply removed and the same steps to estimate $\eta$ were applied.



*Percolation graph for mesoporous catalyst*



*Effectiveness factor* $\eta$ *for mesoporous* (M) *and macroporous catalysts* (H30-H200) *with diameters of macroporii from 30nm to 200nm*

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# ON THE INDUCTION PERIOD OF THE CONVERSION OF METHANOL OVER ZSM-5 CATALYSTS: TRANSIENT STUDIES USING A TAP REACTOR

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An understanding of how the first C-C bond forms from methanol over zeolite catalysts has remained elusive ever since the process discovery in 1977. Although it is well established that a certain "hydrocarbon pool" regulates product distribution[1] at steady state, the origin and evolution of this active pool of species is not yet clearly defined. In this paper, the induction period during which the first C-C bond is formed[2] has been investigated by combining step response experiments, temperature programmed desorption techniques and seeding the catalysts in a temporal analysis of products (TAP) reactor.

10 mg of ZSM-5 catalysts were subjected to multiple cycles of a step response of 5 vol% oxygenate (methanol, DME) between 300 – 450 °C. After steady state was reached, the samples were purged with argon and subjected to temperature programmed desorption (TPD) at 15 $°C\ min^{-1}$ or 25 $°C\ min^{-1}$ up to 470 °C. This TPD of "activated ZSM-5" was compared to individual TPD profiles of species known to be involved in the hydrocarbon pool under TAP conditions. Finally, the ZSM-5 catalyst was seeded separately with 1,5-hexadiene and dimethoxymethane to observe their effect on the induction period.

Ethene and propene are the major olefins formed, with propene being more dominant at lower temperatures and with a DME feed. Monotonic profiles are observed for outlet oxygenates, ethene and $H_2O$ while a sigmoid S-shape profile is obtained for propene at high temperatures. At lower temperatures (< 350 °C), decomposition products ($CH_2O$, CO, $CH_4$ and $H_2$) are released before olefins. Also, a sudden shift in behaviour is observed where an overshoot in $H_2O$ concentration occurs while propene forms when oxygenates and $H_2O$ reach steady state (Fig. 1a). This behaviour is due to the slow generation of active species on the surface of the activated catalyst.[3] Mass, carbon, hydrogen and oxygen balances show an occlusion of hydrocarbons and oxygenates in the ZSM-5 catalysts during step response experiments. Multiple step-up inputs leads to a removal of the induction period observed in the first induction period due to the presence of the active pool of species.

The desorption of this active pool occluded in the ZSM-5 zeolite at ca. 440 °C at a heating rate of 15 °C $min^{-1}$ returns the catalyst to its original state as initial induction periods are generally re-established. A comparison of the desorption profiles of the active pool to the individual desorption profiles of toluene, bibenzyl, methanol, dimethyl ether and olefins show that the active pool does not correspond to the hydrocarbon pool. The desorption profiles of dimethoxymethane and 1,5-hexadiene agree to the desorption profiles of the active pool of species.

Seeding the ZSM-5 catalyst with either 1,5-hexadiene or dimethoxymethane followed by a step response of DME showed a reduction of induction period with dimethoxymethane compared to a pure DME feed alone (Fig. 1b). This leads to the conclusion that, at low pressures and in the absence of coke formation, oxygenates (methanol, DME) lead to decomposition products ($CH_2O$, CO, $CH_4$ and $H_2$) and secondary oxygenates (dimethoxymethane, dimethoxyethane) which subsequently lead to ethene and propene formation through the olefin cycle. Current work is ongoing to obtain a more quantitative understanding of the induction period using transient kinetic modelling techniques.

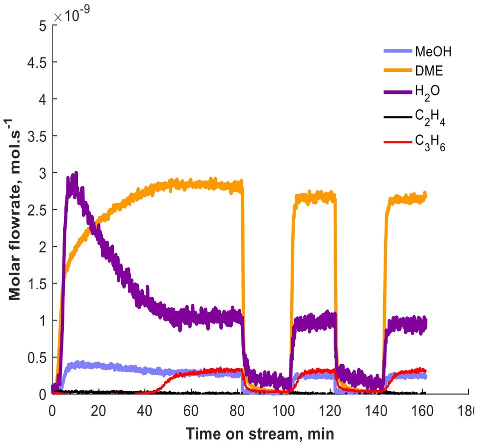

**Fig. 1a**:Step response of 5 vol% DME at 300 °C over ZSM-5 (25) catalysts. Total (cold) molar flow rate (5 vol% DME, balance Ar) = 4.58 × $10^{-8}$ mol $s^{-1}$

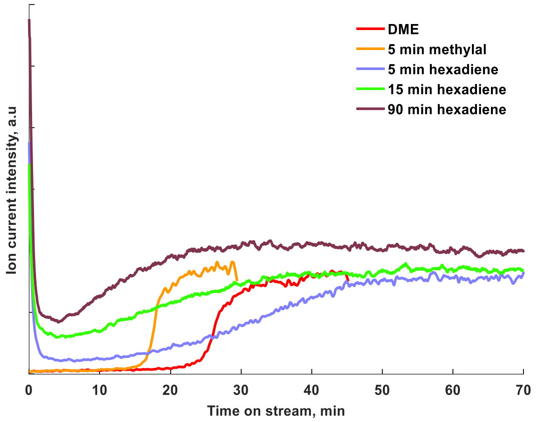

**Fig. 1b**:Comparison of induction times in propene formation with 5 vol% DME in argon only (-), after introduction of a step response of 2.5 vol% 1,5-hexadiene for 5 (-), 15 (-) and 90 (-) min followed by a step response of 5 vol% DME in argon, after introduction of a step response of 5 vol% methylal for 5 min followed by a step response of 5 vol% DME in argon (-) over ZSM-5 (11.5).

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# NEW INSIGHTS IN CHEMICAL RELAXATION:
# INVARIANTS AND CONSERVATIVELY PERTURBED EQUILIBRIUM

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Searching for invariants is one of the most important goals in many sciences such as chemical kinetics and chemical engineering [1-3]. Invariants are functions of state variables that remain constant during the non-steady-state transformations.

There are two well-known linear invariants that are widely used in chemistry and chemical engineering [4, 5]:

- Linear element conservation laws.
- Linear stoichiometric relationships.

Since 2011, other invariants of thermodynamic origin for first-order, reversible reactions have been found [6-9]. They are related to the famous Onsager's reciprocal relations [10, 11]. For linear or linearized kinetics (dx/dt) = Kx, with microreversibility, the kinetic operator K is symmetric in the entropic inner product. This form of Onsager's reciprocal relations implies that the shift in time, exp(Kt), is also a symmetric operator. This generates the reciprocity relations between the kinetic curves, and the ratio of dual kinetic dependences coincides with the equilibrium constant. It was proven experimentally using the catalytic water-gas-shift (WGS) reaction [7]. In this paper new invariants of non-thermodynamic nature for the given mechanism, the two-step consecutive mechanism A↔B↔C, are presented. These invariants, specific for the given mechanism, are ratios of linear combinations of concentration dependences which are started from the initial states with only a single component. The invariant expression is based on the '*Scaled Incremental Conversion*' (SIC), denoted $\chi$, i.e. a function of modified conversions of different components. For the analyzed mechanism, the invariant is determined by four SIC expressions at initial conditions with only a single component A, B or C.

For the case of initial state with some equilibrium concentration(s) as initial one(s) and at the same amounts of given elements, the concept of the "conservatively perturbed equilibrium" was formulated, see Fig. 1. Obviously, the relaxation to the detailed equilibrium is characterized by the unavoidable extremum (maximum or minimum). Characteristics of such extrema are presented for the Wei-Prater triangular mechanism [6]. It was shown that the extremum time is independent on the initial reaction conditions.

Based on the perturbed equilibrium procedure, some mechanistic details can be extracted and kinetic parameters can be estimated.

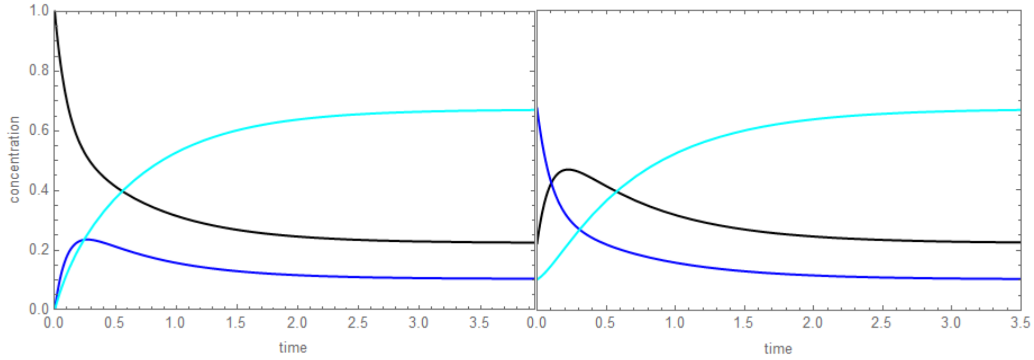

**Fig. 1-** Concentration profiles of A (black), B (blue) and C (cyan) in a two-step consecutive mechanism $A \leftrightarrow B \leftrightarrow C$, in the left side, starting from pure A, $(A_o, B_o, C_o) = (1, 0, 0)$, and, in the right side, starting from the crossed equilibrium concentrations of B and C, with A in conservatively perturbed equilibrium, $(A_o, B_o, C_o) = (A_{eq}, C_{eq}, B_{eq})$.

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# ON TERMOLECULAR REVERSIBLE REACTION KINETICS: TYPICAL DEPENDENCIES EXPLAINED WITH AUTOCATALYTIC REACTIONS

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Generally, the occurrences of termolecular elementary reactions are assumed to be rare and this mechanism is often disregarded when studying the kinetics of processes with overall third order rate laws. However, termolecular elementary reactions may be more common than previously assumed, if the notion of instantaneous collision-time is disregarded. A collision between three particles may then take place during the time interval of two particles colliding. A third particle collides with the initial two particle collision possibly resulting in a termolecular reaction. Thus it is interesting to take a closer look at termolecular elementary reactions.

In the context of this work, only reversible termolecular reactions in a closed system where considered. The kinetics of reversible termolecular reactions were shown to be mathematically equivalent to the kinetics of reversible autocatalytic reactions. It could be proven that the kinetics of any third order or lower reaction within a closed system can be described as a multi-reaction mechanism of third order autocatalytic reactions within a similar closed system.

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# KINETIC MONTE CARLO MODELING OF PULSED LASER (CO)POLYMERIZATION TO DETERMINE INTRINSIC RATE COEFFICIENTS

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Pulsed laser polymerization (PLP) is one of the most interesting techniques to study individual reactions in radical (co)polymerization [1]. In PLP, photoinitiator radicals are generated at laser pulses with a frequency $v$ (or dark time $\Delta t = v^{-1}$). Depending on the PLP conditions and the monomer type, the molar mass distribution (MMD) can possess specific characteristics, allowing the determination of intrinsic rate coefficients. Most known is that under well-chosen conditions a multimodal MMD with inflection points $L_j$ ($j$ = 1, 2, …) is obtained, allowing the determination of the propagation rate coefficient $k_p$ ($[M]_0$: initial monomer concentration):

$$k_p = L_j\,(j\Delta t)^{-1}\,[M]_0^{-1} \qquad (1)$$

In this contribution, kinetic Monte Carlo (*k*MC) modeling is applied to allow a further understanding and exploitation of PLP. For PLP of acrylates, regression analysis to low frequency inflection point data at various solvent volume fractions is proposed as a new method to estimate the backbiting (Figure 1; middle) [2] and β-scission rate coefficient [3].

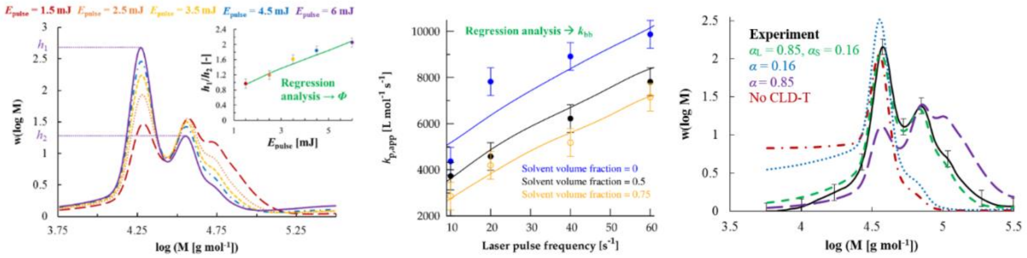

**Figure 1. PLP applied for the estimation of $\Phi$ (left) and $k_{bb}$ (middle), and benchmarking of $k_{t,app}$ models (right).**

Moreover, it is demonstrated that photodissociation, chain initiation and termination reactivities can be extracted from the complete PLP MMD [4]. For the first time, the ratio of MMD peak heights has been used for the fast and reliable estimation of the photodissociation quantum yield $\Phi$ (Figure 1; left) [5]. In addition, typically used models for the apparent termination reactivity $k_{t,app}$ are benchmarked at low monomer conversions (Figure 1; right), *i.e.* conditions not easily accessible with other techniques such as the RAFT-CLD-T technique.

For PLP of vinyl acetate a unique combination of *ab initio* calculated rate coefficients and *k*MC simulations is considered to explain the experimental [6] $v$ dependency of the observed $k_p$ (Equation (1)). Via a stepwise extension of the *k*MC model, the $v$ dependency is attributed to backbiting of tail radicals formed via head-to-head propagation [7].

The PLP technique is also used for the estimation of cross-propagation rate coefficients in radical copolymerization and for the evaluation of the importance of penultimate unit effects. Kinetic Monte Carlo modeling of acrylate pulsed laser copolymerization is applied for the identification of PLP conditions allowing the determination of ECR cross-propagation rate coefficients.

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# FINITE ELEMENT SOLUTIONS TO REACTION-DIFFUSION PROBLEMS WITH DEAD-CORES

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The dead-core phenomena frequently occur in catalytic reaction engineering. In those cases the amount of a reactant provided by the diffusion flux is not able to compensate its consumption. Therefore, zones with no reaction can be formed. The localization of such dead-cores is useful in order to reduce the expenses for catalyst and to control the reaction process. In this paper we present stable finite element schemes to solve reactor problems with dead-cores occurring inside the reactor domain or on the catalytic membrane boundary part as well. Our approach based on the composite finite elements [1] is successfully applied to solve boundary value problems with nonlinear reaction terms that are non-differentiable at zero. The standard iteration methods fail when solving such class of nonlinear boundary value problems. In order to reach the steady-state solution, we apply the variational time marching method [2] which leads to the minimization of the corresponding energy functionals. Our error analysis is justified by numerical tests for problems possessing dead-core solutions.

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# Experimental study of the intrinsic kinetics of steam methane reforming on a thin Ni coating

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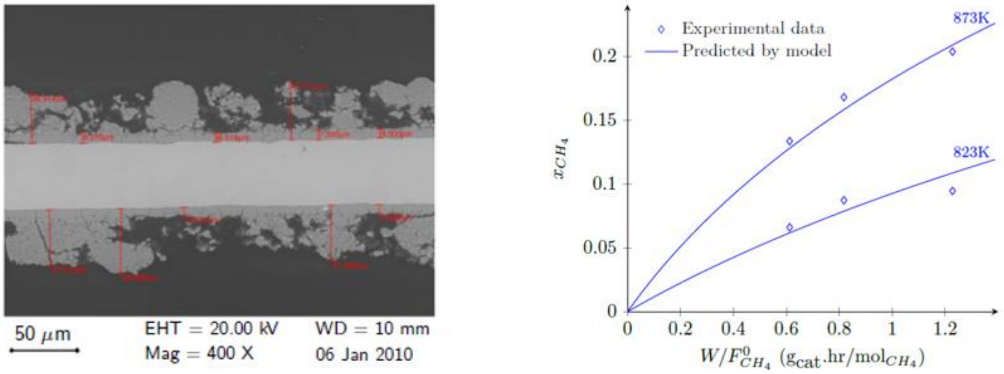
Structured catalytic reactors have shown potential to intensify catalytic processes. When properly designed, an optimized flow pattern allows increased heat transfer efficiency and reduced pressure drop compared to conventional packed bed reactors [1-2]. The use of a thin catalyst coating allows increased effectiveness factors. But the application of such a coating that is expected to be stable under severe operating conditions is challenging. Alloy Surfaces Co. Inc. developed an intrinsically bound thin-layered catalyst adhered on a metal substrate. The material has a uniform coating thickness which allows physical structuring into the desired geometry and avoiding a posteriori washcoating [3]. The intrinsic kinetics of steam methane reforming and water-gas shift reactions were experimentally studied on this new catalyst.

The experiments were carried out in a tubular packed bed micro-reactor. The reactor was designed and operating conditions selected to have plug flow, isothermal operation, negligible pressure drop and negligible interfacial and intra-particle transport limitations [4]. Methane steam reforming experiments were carried out at temperature ranging from 450 and 600°C, pressure between 1 and 25 bars and steam-to-carbon ratios between 3 and 5. Hydrogen was co-fed and the catalyst bed diluted to guarantee isothermal operation. Methanation and reverse of water-gas shift experiments were performed at temperatures between 300 and 450°C and pressure between 1 and 25 bars. Different reaction mechanisms with potential rate determining steps were investigated and rate equations were derived following the Langmuir-Hinshelwood-Hougen-Watson approach. Estimation of the rate parameters was made by linear and non-linear regression. The models containing non-physically meaningful parameters were eliminated. Discrimination between the remaining models followed from statistical testing, based on F-test and $R^2$ value [5-6]. Comparison with a conventional SMR catalyst was made [7-9]. Intra-catalyst diffusion limitations were investigated based on the pseudo-continuum model and the optimal catalyst coating thickness was evaluated [10].



(a) (b)

*Figure 1: (a) SEM cross section of the catalyst and (b) molar conversion of methane versus space time at 3 bar and S/C = 3.5.*

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# Data quality assessment by clustering analysis and principle component analysis

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The process of model development and model analysis is often limited by the availability of suitable experimental data, as the validation step is, in general, conducted based on that data [1]. While, this approach is the basis for modelling, care has to be taken that the experimental data is trustworthy and resembles the reality accurately. Unfortunately this step is often overlooked.

In this contribution, a tool, the "ExpSimVisualiser", is presented to automatically process, evaluate and store experimental yield data. The tool creates an HDF5 [2] file containing all relevant data of the experiment and enables through visual representations of the obtained results, a fast and objective measure of the data's quality. In total 11 graphs are plotted that give information on the conservation of mass and chemical elements, data stability and consistency, and the correlation of every species-pair. The correlations coefficients can throw light upon the underlying reaction pathways.

The similarity of the datapoints is assessed through the combined use of Principal Component Analysis (PCA) [3] and Mahalanobis distances [4, 5]. PCA is a multivariate statistical technique that allows to project the information carried by the original variables onto an equal or smaller number of uncorrelated variables, while preserving the most important information (maximal variance) [3]. The "ExpSimVisualiser" converts the multidimensional data matrix $X$ of n (observations) × k (variables = species) to $T$ of n × 2 for human interpretable two-dimensional visualization. PCA can be represented by Eq 1 where $T$ is the score matrix, $P$ represents the loading matrix and $E$ the residual matrix. Similar datapoints projected onto the new coordinate system will be clustered together. Confidence intervals of 70, 80 and 95 % around those clusters are drawn based on the respective Mahalanobis distances for unambiguous outlier detection. The two-dimensional score plot of the first and second principal component entails on average > 99 % of the variance of the original yield dataset and conclusions drawn from the score plot can thus be confidently extended over the complete dataset

$$X = TP^T + E \qquad \text{Eq 1}$$

The HDF5 file contains all information to automatically start simulations and the tool can automatically compare the results with the experiments. To circumvent the problem of different identifiers for different components, an unique identifier, IUPAC InChI [6], is employed as underlying infrastructure for storing component names.

Although the presented tool is written for kinetic yield data specifically, the data quality assessment is more generally applicable. The “ExpSimVisualiser” can thus be a vital tool in modelling projects wherein large data are utilized.

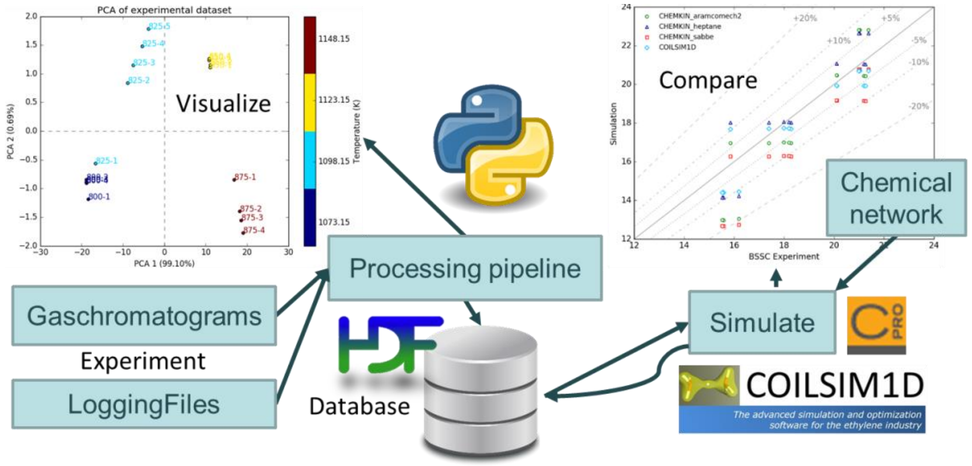

**Figure 1:** Schematic overview of the processing pipeline of the ‘ExpSimVisualiser’. Evaluation of yields through PCA (graph left). Parity plot of experiment versus simulation (graph right).

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# Multi-scale modeling of an annular structured catalytic reactor: application to steam methane reforming

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Structured catalytic reactors have shown potential to intensify catalytic processes. An optimized flow pattern allows increased heat transfer and reduced pressure drop compared to conventional packed bed reactors [1-2]. A thin layer of catalyst is coated on the internals of the reactor, allowing high catalyst effectiveness factors. Reactor design, optimization and scale-up requires the development of a detailed reactor model accounting for intrinsic reaction kinetics and transport phenomena. A multi-scale approach is presented for the case of an annular structured reactor for methane steam reforming (ZoneFlow™ Reactor Technologies).

The intrinsic kinetics of steam methane reforming and water-gas shift reactions on a new Ni-based, intrinsically bound thin-layered catalyst adhered on a metal substrate were experimentally studied [3]. The experiments were performed in a tubular packed bed micro-reactor, designed to avoid transport phenomena limitations [4]. Estimation of the parameters and discrimination between the competing models followed from non-linear regression and statistical and physicochemical testing [5-7]. Intra-catalyst diffusion limitations were accounted for using a pseudo-continuum model [8].

The commercial reactor performance is also determined by the complex flow pattern. A Computational Fluid Dynamics (CFD) model was developed. The Reynolds-Averaged Navier-Stokes (RANS) approach was adopted and turbulence was accounted for through the k-ε model. Thermal conduction in the walls and the internals of the reactor was accounted for and radiation was described by means of the Rosseland-Weighted Sum of Gray Gases Model. The CFD code was coupled with the intrinsic kinetic model and effectiveness factors independently calculated were imposed. The model parameters were determined from a combination of cold flow pressure drop tests and hot inert and reactive flow tests in different pilot plant units. The complete model was finally used to perform simulations of a commercial steam reformer. Comparison with a conventional packed bed reactor is made [8-10] to demonstrate the process intensification potential of the annular structured reactor.

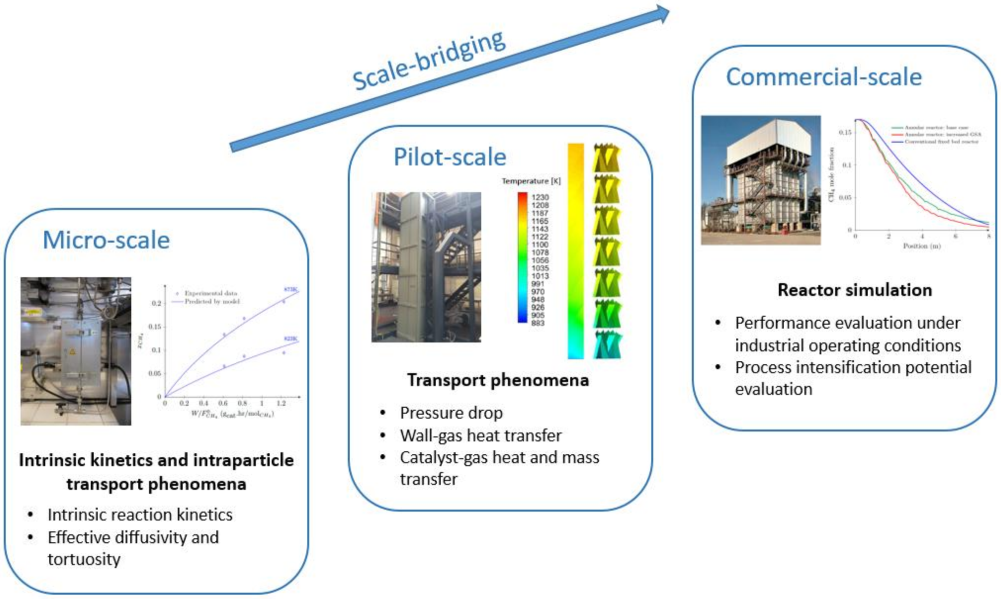

*Figure 1: Multi-scale approach for the development of a reactor model.*

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# Exploring Chemical Reaction Networks with KiNetX

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A tool for automated quantum mechanical exploration of molecular reactivity previously published by our group, Chemoton [1], generates complex chemical reaction networks and associated properties such as activation energies. The size of the networks quickly becomes intractable, in particular if the involved species cause multiple side reactions. Then, the relevant kinetics of a chemical species might be hidden under a myriad of reactive conformers. For a kinetic analysis, the chemical reaction network must be converted to a set of possibly stiff ordinary differential equations (ODE). Ideally, the resulting chemical kinetics analysis is then carried out under full error control. KiNetX [2] is a C++ software aimed at the analysis of complex chemical reaction networks and their efficient exploration. Our software has been developed to possess four features. It is able to convert the graph structure of the network into a set of ODE and to identify and prune kinetically irrelevant species. Moreover, it propagates the first-principle uncertainty in activation energies estimated by Chemoton [3] as uncertainty in concentration trajectories. Most importantly, it collects the knowledge acquired through this analysis and drives the chemical reaction network exploration of Chemoton, for instance, avoiding wasting resources exploring kinetically irrelevant portions of the graph or identifying critical paths where more refined calculation methods should be employed.

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# Mathematical modeling of network polymers

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Early mathematical models for linear polymer synthesis via step-growth and chain-growth have been developed by Schulz[1], Flory[2], Stockmayer[3] and others. These models typically assume exclusively intermolecular reactions and start to break down when the polymerization reactions take place intramolecularly, *e.g.* when forming network polymers. Nonetheless, such network polymerizations are important synthetic routes toward high-tech biomedical and pharmaceutical applications, *e.g.* biocompatible carriers for site-specific drug delivery. A major challenge for next-generation biocompatible carriers is understanding the effect of the macromolecular architecture of 3-dimensional polymer gels on product performance. It is believed that macromolecular architectures characterized by homogeneous composition and controlled/narrow pore size distribution improve thermal, mechanical and swelling properties of polymer gels. Mathematical modeling allows to efficiently identify reaction conditions leading to the desired macromolecular architecture. While kinetic modeling studies exist for chain-growth reactions forming network polymers, *e.g.* free radical polymerization of styrene in the presence of divinylbenzene, detailed modeling efforts for highly cross-linked network polymers via step-growth polymerizations have not been reported.

In this contribution, a novel modeling tool is presented, based on the kinetic Monte Carlo technique, to predict the temporal evolution of the polymeric architecture of 3-dimensional polymer networks via both chain-growth and step-growth mechanisms. As a case study, the para-fluoro-thiol reaction (PFTR), a nucleophilic substitution reaction between a pentafluorobenzyl group and a thiol derivative[5], is presented. The developed model is benchmarked against dedicated experimental data, featuring both equimolar and non-equimolar reactions conditions, allowing fairly accurate determination of model parameters and achieving a good agreement between experiment and prediction. On a longer term, the predictive capabilities of the model should allow model-based design of hydrogels, offering unique opportunities for biomedical and pharmaceutical applications.

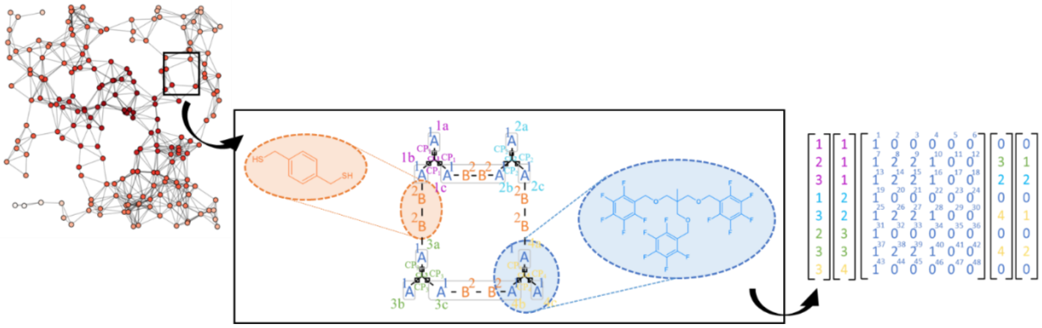

Figure 1. Modeling the macromolecular architecture of network polymers synthesized via a para-fluoro-thiol reaction.

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# Stochastic simulation of MADIX/RAFT polymerization at the molecular level

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The production of core-shell nanostructured polymeric latexes via Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization, also known as MAcromolecular Design via the Interchange of Xanthates (MADIX) polymerization, is a multi-scale industrial design challenge. Specifically for nitroxide mediated polymerization in aqueous miniemulsion, such complex interplay between microscale (chemical kinetics) and mesoscale (phase partitioning of the mediating agent) phenomena has already been reported [1]. For RAFT polymerization in aqueous emulsions, similar interplay between microscale and mesoscale can be expected. Hence, in this contribution, a dedicated micro-scale modeling study is presented, accurately modeling the RAFT/MADIX kinetics on the molecular level and under bulk conditions, unperturbed by any mesoscale effects related to the presence of an aqueous phase. A deterministic modeling technique is used to predict the MADIX polymerization kinetics of styrene and its chain extension with n-butyl acrylate (nBuA) toward the synthesis of block copolymers (which are ultimately required for the desired core-shell morphology). Azobisisobutyronitrile (AIBN) is chosen as the conventional radical initiator and O-ethylxanthyl ethyl propionate (OEXEP) as the RAFT agent ($R_0X$). Degenerative chain transfer (exchange) constants for both exchange with $R_0X$ ($C_{tr,0} = 0.80 \pm 0.02$) and macro-RAFT agent ($C_{tr} = 0.44 \pm 0.07$) are determined via multi-response regression analysis to the experimental data on the RAFT agent and styrene conversion, number and mass average molar masses, and end-group functionality (EGF). The EGF data are obtained by a novel procedure involving dialysis to remove residual $R_0X$ species and elemental analysis. The numerical difference between the $C_{tr}$ and $C_{tr,0}$ values is important for the prediction of the experimental responses: explicitly acknowledging the differences in these exchange reactivities, reveals that, for the selected conditions, the chain length of the polystyrene radicals obeys the Schulz-Flory distribution. Similarly, for the chain extension with nBuA, the segment length of the nBuA block also obeys the Schulz-Flory distribution. Hence, in contrast to typical RAFT polymerizations, each individual block of the copolymer obeys the Schulz-Flory distribution. This insight in the MADIX mechanism, *i.e.* each block of the copolymer being formed through approximately a single series of propagation steps followed by a single exchange reaction event, is confirmed using a stochastic modeling approach predicting and visualizing the temporal evolution of the chain length and block length of the individual copolymer chains. The latter allows to rank blockpolymer products according to a quality index based on monomer sequence length and end-groups, and ultimately, the design of future generations of RAFT agents suitable for the industrial production of nanostructured polymeric latexes.

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# Kinetic modeling of selective oxidation of $H_2S$ on $Fe_2O_3/Cr_2O_3/Al_2O_3$

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## Abstract

Claus process is used for sulfur recovery in oil and natural gas refineries. SuperClaus process can increase the sulfur recovery and reduce the environmental problem of the Claus process by adding selective oxidation reaction. This reaction was developed base on different catalyst experimentally. But kinetic model and rate of the reactions have not been developed yet that are necessary for simulation the process. In this article, a reaction network including main and side reactions was developed. Reaction constants and activation energies of this model were fitted using nonlinear optimization on set of ordinary equations of plug flow reactor. The results show good agreement between $H_2S$ conversion and sulfur selectivity according to different temperatures. The coefficient of determination, $R^2$, of nonlinear regression for the conversion and selectivity are 0.989 and 0.975, respectively.

**Keywords:** SuperClaus, Kinetic modeling, selective oxidation, $H_2S$

## 1. Introduction

The Sulfur Recovery Unit (SRU) has been developed in the oil and gas industry to prevent the release of toxic and harmful sulfur compounds to the environment. The Claus process is one of the major processes used to convert $H_2S$ gas to sulfur in the process of refining sour gas in the refineries [1]. The Claus process consists of two sections including thermal section before catalytic section. The catalyst section usually contains 2 or 3 reactors that produce elemental sulfur by reacting of $H_2S$ (unreacted in the thermal section) and the $SO_2$ (produced from the thermal section) [2]. In the Claus process, the highest sulfur recovery rate will be 98%, but the SuperClaus process, which is a new process, will result in a recovery rate of more than 99% by selective oxidation. In this process, a selective oxidation reactor is added [3]. For selective oxidation of $H_2S$, two types of catalysts are mainly used: 1. Carbon based catalysts, which are mainly used for discontinuous processes at low temperatures. 2. Metal based catalysts that are mostly used [4]. Experimental works have been carried out in this regard, but so far no kinetic model has been presented. In this paper, a kinetic model for selective oxidation of hydrogen sulfide is developed using experimental results of ref. [5] for $Fe_2O_3/Cr_2O_3/Al_2O_3$ catalyst.

## 2. Model

A reaction network including three reactions was considered for selective oxidation of $H_2S$ according to Equation (1)-(4). Reaction (1) is the target reaction for oxidizing $H_2S$ to sulfur and the others are side reactions that reduce the selectivity.

Reaction rates of this model were summarized in Equation (5)-(6) for reaction (1)-(4), respectively. Partial mole balance for the $i^{th}$ component in the plug flow reactor was presented in Equation (9). This set of ordinary differential equations was solved numerically using Matlab software. For finding reaction rate constants and activation energies, the Nelder-Mead simplex algorithm was used in Matlab. The objective function contains weighted sum of absolute of errors for conversion and selectivity which errors are difference between model and experiments data.

$$2H_2S + O_2 \leftrightarrow S_2 + 2H_2O \quad (1)$$

$$r_1 = k_{10f}\left(exp\left(\frac{-Ea_{1f}}{RT}\right)P_{H_2S}^2 P_{O_2} - (1/K_{eq})exp\left(\frac{-Ea_{1b}}{RT}\right)P_{S_2}P_{H_2O}^2\right) \quad (5)$$

$$S_2 + 2O_2 \rightarrow SO_2 \quad (2)$$

$$r_2 = k_{20}exp\left(\frac{-Ea_2}{RT}\right)P_{S_2}P_{O_2}^2 \quad (6)$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \quad (3)$$

$$r_3 = k_{30}exp\left(\frac{-Ea_3}{RT}\right)P_{H_2S}^2 P_{O_2}^3 \quad (7)$$

$$3S_2 + 4H_2O \rightarrow 4H_2O + 2SO_2 \quad (4)$$

$$r_4 = k_{40}exp\left(\frac{-Ea_4}{RT}\right)P_{S_2}^3 P_{H_2O}^4 \quad (8)$$

$$\frac{dF_i}{dV} = \boldsymbol{\rho_b} \sum_{\boldsymbol{j=1}}^{\boldsymbol{N_{R=4}}} \boldsymbol{\alpha_{ij}\, r_j} \quad (9)$$

## 3. Results and Discussion

After fitting the parameters of the model, $H_2S$ conversion and sulfur selectivity of the model and the experiments were compared in the Figure 1. The results show good mathematical fitting. The errors are in the range of uncertainty of experimental data in forward heating and cooling data of ref. [5]. The coefficient of determination, $R^2$, of nonlinear regression for the conversion and selectivity are 0.989 and 0.975, respectively that confirmed the suitable curve fitting algorithm and presented reaction network and the kinetic models for each reaction rate.

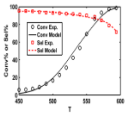

Figure 1. Comparing $H_2S$ conversion and sulfur selectivity in the model and experimental results v.s. reaction temperature.

## 3. Conclusions

For the first time a kinetic model was presented for selective oxidation of $H_2S$ $Fe_2O_3/Cr_2O_3/Al_2O_3$. The presented kinetic model has good agreement with experimental results. This kinetic model can be used for SuperClaus process simulation that is more precise than Equilibrium and Gibbs reactor models.

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# KINETIC MODELING OF HYDROGEN PRODUCTION BY DARK FERMENTATION

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Hydrogen is one of the cleanest energy carriers and its localized production for mobility or for energy production is a current issue. To ensure sustainable production, production pathways from biological processes (photo or dark fermentation) other than conventional fossil hydrocarbon reforming pathways are studied [1]. For photofermentation, photosynthetic bacteria need light to convert organic compounds into hydrogen and other by-products, while dark fermentation has the advantage to produce hydrogen in the absence of light and oxygen from biodegradable waste by an anaerobic bacterial consortium [2]. Several models have been proposed and developed to describe the metabolism of fermentation [3].

This work uses a kinetic model to describe the initial loading conditions of biomass selected to produce hydrogen with high yields and also to find the variation of bacteria growth in the reaction medium. A vinicultural biomass (grape residues) without exogenous inoculum was implemented in a semi-batch reactor. A non-linear kinetic model was proposed to describe the production of hydrogen and other fermentation products (organic acids, alcohols), the consumption of substrates contained in the biomass as well as its growth during fermentation. Different metabolic pathway schema have been proposed to find the most appropriate model to describe all metabolic pathways of bacteria found in the medium.

The modeling procedure was divided in two steps. Firstly, determine the model and kinetic parameters using the Trust-Region-Reflective optimization algorithm in MATLAB package optimization algorithm to fit the equations coupled to the kinetic expressions with the fourth Runge-Kutta for integrating differential equations. Experimental profiles were used to adjust the model and kinetic parameters.

Secondly, the proposed kinetic model was used to predict the initial conditions of the biomass selected to produce biohydrogen by dark fermentation using the previously obtained parameters. The describing equation of hydrogen production is:

$$\frac{dH_2}{dt} = \left[\frac{Y_{H_2-S}}{Y_S} * \sum R_{PS} - \sum Rc + \frac{Y_{H_2-T}}{Y_T} * \sum R_{PT}\right] * \left[1 - e^{-\frac{S+T}{Ki}}\right]$$

where $Y_{H_2-S}$ and $Y_{H_2-T}$ are yield of hydrogen production from sugar and tartrate, $Y_S$ and $Y_T$ are yield of degradation and consumption of sugar and tartrate, $R_{PS}$ and $R_{PT}$ are kinetics of production of hydrogen from sugar and tartrate, $Rc$ is a kinetics that inhibits hydrogen production and $Ki$ is an inhibition constant.

The results of optimization modeling are presented in Figure 1.

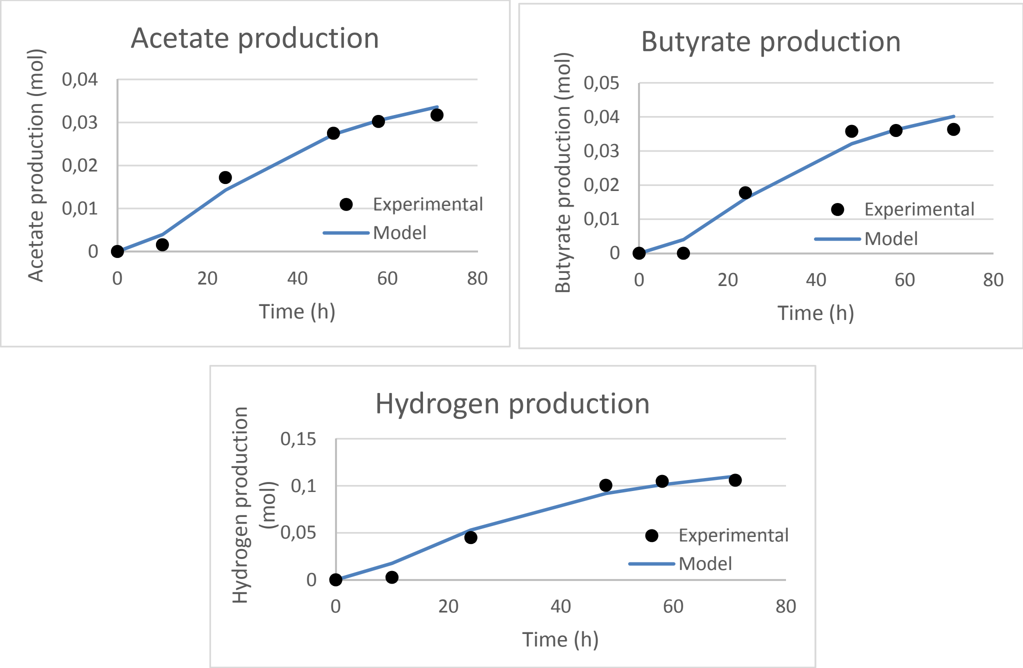

**Figure 1.** Experimental and model simulation profiles of acetate, butyrate and hydrogen production

The simulation results indicate that the proposed kinetic model can well describe hydrogen and other metabolite production by dark fermentation.

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# Low-temperature steam reforming of light hydrocarbons: kinetic study on the way to selective conversion

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Nowadays there is a problem of associated petroleum gas (APG) processing in Russia, Nigeria, Saudi Arabia and north states of USA. Typical APG composition is (vol. %) 50-70 $CH_4$, 5-10 $C_2H_6$, 10-30 $C_{3+}$-hydrocarbons (up to octane), 0-10 $N_2$, 0-10 $CO_2$. Due to the presence of $C_{3+}$-fraction, APG causes engine damage and therefore can not be used as a fuel to generate electricity directly at oil fields. APG also has high hydrocarbon dew point and can not be transported by conventional gas pipelines. Thus, an alternative way of APG utilization is necessary.

Low temperature steam reforming (LTSR) of APG represents a promising method of APG utilization. The process occurs at 250-350 °C and low steam to carbon ratio ($H_2O/C_{C2+}$ mol. < 1). Overall process can be described by two reactions: irreversible steam reforming of $C_{2+}$-hydrocarbons with the formation of $CO_2$ and $H_2$ followed by reversible $CO_2$ methanation:

$$C_nH_{2n+2} + 2nH_2O \rightarrow (3n+1)H_2 + nCO_2 \quad (n > 1) \tag{1}$$

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \tag{2}$$

It was shown that reactivity of $C_2$-$C_5$ hydrocarbons increases with its molecular mass (Fig. 1). Converted APG with high methane content meet the requirements for natural gas: net calorific values are higher than 31.8 MJ/m$^3$ and Wobbe indexes are between 41.2 and 54.5 MJ/m$^3$. Reaction orders with respect to $C_2$-$C_5$ hydrocarbons are close to one. Reaction order with respect to steam is slightly negative or close to zero. Concentrations of $CH_4$, $CO_2$ and $H_2$ do not significantly affect the hydrocarbon conversion. Effective activation energies for $C_2$-$C_5$ LTSR range from 115 to 150 kJ/mol. Comparing the values of reaction quotient ($Q_r$) and equilibrium constant ($K_P$) at different temperatures (Fig. 2), we showed that $CO_2$ methanation occurs in quasi-equilibrium mode at temperature above 250 °C so overall process rate is limited by the reaction of $C_2$-$C_5$ hydrocarbons steam reforming. Ni catalysts are not subjected to carbon deposition under the reaction conditions despite this side process being thermodynamically possible.

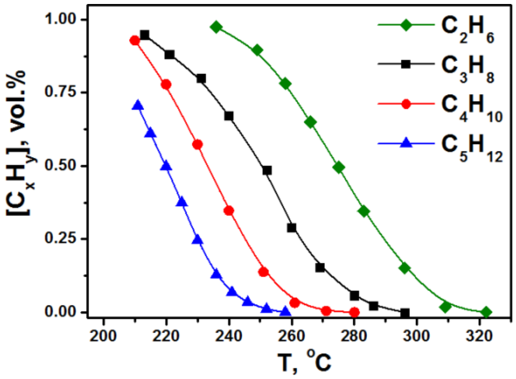

Fig. 1. Temperature dependencies of outlet concentrations (on dry basis) for steam reforming of $C_2H_6$, $C_3H_8$, $C_4H_{10}$ and $C_5H_{12}$. Inlet gas mixture (vol. %): 58.4 $CH_4$, 0.6 $C_nH_{2n+2}$, 41 $H_2O$. P = 1 bar, GHSV = 3000 $h^{-1}$.

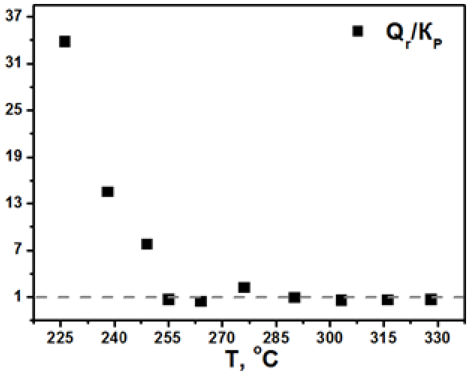

Fig. 2. $Q_r/K_P$ at different T for LTSR of a complex $C_2$-$C_5$ mixture. Inlet gas (vol. %): 45.9 $CH_4$, 9.3 $C_2H_6$, 5.9 $C_3H_8$, 2.9 $C_4H_{10}$, 0.7 $C_5H_{12}$, 35.2 $H_2O$. P = 1 bar, GHSV = 2600 $h^{-1}$.

Based on the novel results obtained, we suggest an extended macrokinetic model which consists of reactions of hydrocarbons steam reforming, hydrocarbons hydrogenolysis and quasi-equilibrium reaction of $CO_2$ methanation. Fig. 3 shows comparison between simulation results and the experimental data on the LTSR methane-propane and methane-butane. This simple macrokinetic model correctly describes the experimental data and can be used for catalytic reactor design in perspective. The introduction of hydrogenolysis to the model provided correct description of low-temperature region.

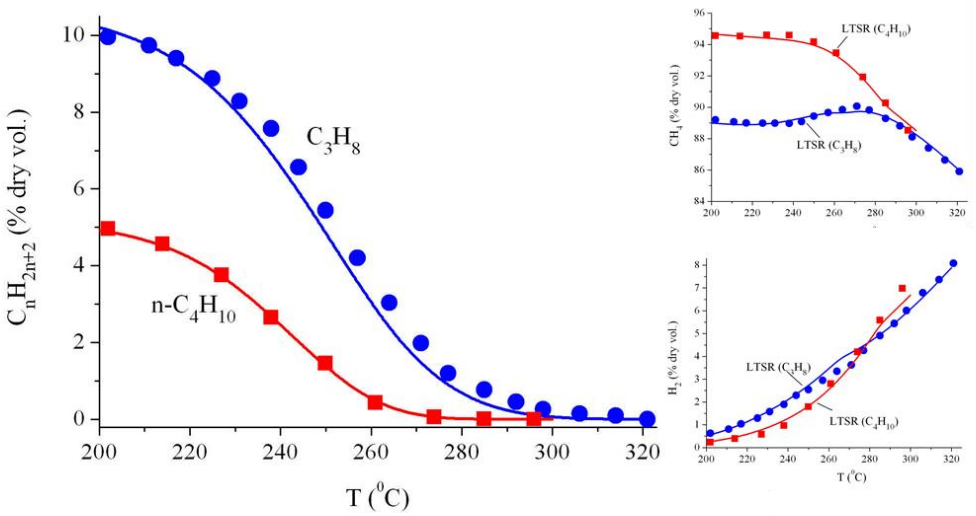

Fig. 3. The temperature dependencies of propane, butane, methane and hydrogen outlet concentrations (on dry basis) in the LTSR of model gas mixtures. P = 1 bar, GHSV = 1800 $h^{-1}$. Points are experiment, lines are simulation.

# Kinetics of Cellulose and Hemicellulose Hydrolysis

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In this work we study the hydrolysis and the equilibrium composition using glucose, xylose and oligomers thereof as starting components. Kinetic models based on population balances [1,2] are fitted to experimental data. The xylane hydrolysis can be achieved at fairly mild conditions compared to cellulose. Further, xylose stability is lower than glucose stability. A separate hydrolysis of hemicelluloses and cellulose is feasible:

i) Hemicellulose is hydrolysed at low acid concentrations, where cellulose is kept in polymer form.
ii) Bonds involving glucose are hydrolyzed at significantly lower rates, which makes it possible to separate the main amounts of xylose from glucose during hemicelluloses hydrolysis.
iii) End groups have a higher activation energy of hydrolysis.

As the solubility of pentoses and oligomers thereof is significantly higher than hexo-oligomers, stepwise dissolution and hydrolysis can be used to achieve hydrolysates with sugar concentrations of higher than 10 wt%. At the conditions for hemicellulose hydrolysis cellulose will still hydrolyze under these conditions. The process is, however, a liquid-solid process and, thus, very slow compared to hemicellulose hydrolysis. The kinetic mechanism for cellulose hydrolysis is shown in Figure 1. The network for hemicellulose hydrolysis is similar with the only difference that instead of anhydroglucose protonated xylose is produced from the dimer and monomer.

Simulations of cellulose and hemicellulose hydrolysis were performed for a wide range of conditions varying the temperature, the sugar concentrations and the amount of HCl. For both cellulose and hemicellulose hydrolysis higher temperatures and lower acid concentrations are favorable to increase the amount of oligomers and, at the same time, reduce the degradation of glucose. Cellulose and hemicellulose should not be hydrolyzed simultaneously, due to the lower stability of xylose compared to glucose. To shift the equilibrium to the monomeric side, rather higher temperatures between 65 ºC and 90 ºC and lower sugar concentrations should be used. The rates can be compensated using less HCl. For residence times of around 1 h HCl amounts of around 1.0-1.5 wt% should be used.

Based on the experimentally obtained kinetic data the optimal conditions for hydrolysis of cellulose and hemicellulose were simulated in Figure 3. We kept the initial amounts of cellulose and xylane constant at a concentration of 8 wt%. It is further assumed that this amount is completely dissolved at the start of the reaction. We set two targets of first to maximize the amount of glucose, while keeping the degradation low. Secondly we will aim to produce a large amount of oligomers, with unit sizes from 2 to 8, which have potential in food applications.

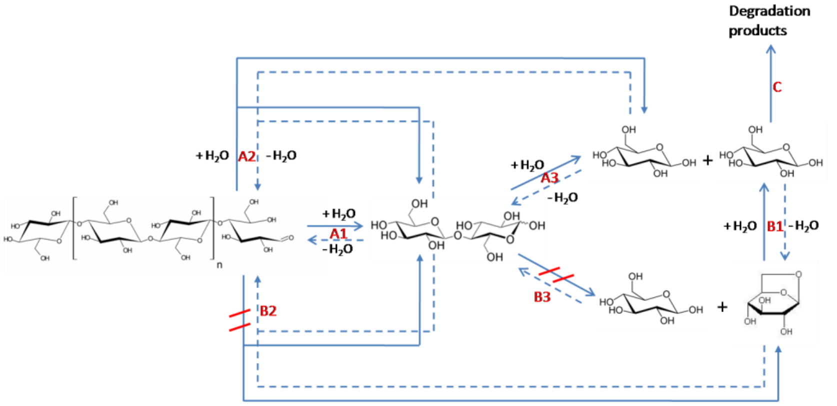

Figure 1: Reaction mechanism for cellulose hydrolysis including dehydration to 5-HMF and further degradation to humins.

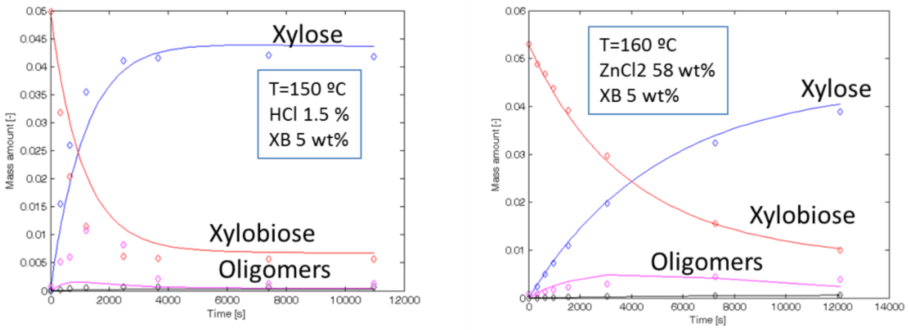

Figure 2: Comparison of xylobiose conversion showing a good fit between experimental data (symbols) and simulation (lines).

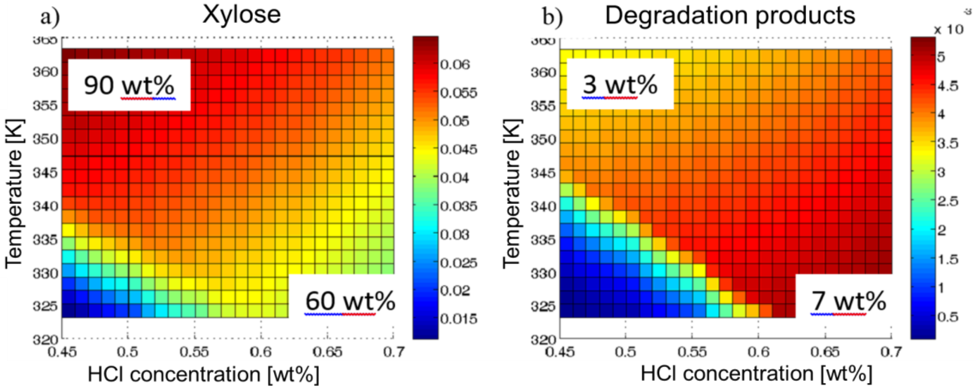

Figure 3: Yields of xylose and degradation products for residence times up to 3 h.

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# AN EFFICIENT APPROACH TO KINETIC PARAMETER ESTIMATION THROUGH DYNAMIC-MODEL-BASED DESIGN OF EXPERIMENT

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Keywords: design of experiment, kinetics, dynamic model, three phases

The conventional kinetic study is time consuming mainly due to two reasons: (1) data is typically recorded after a certain duration when the reactor reaches steady-state conditions; sufficient data is required to achieve an acceptable precision because a part of data provides limited information. By contrast, a dynamic model can fit the data at any time. There is significant body of literature in process chemistry on the use of dynamical reaction data for identification of reaction mechanisms and generation of kinetic models, see e.g., [1]. Design of experiment (DoE) can further enhance the methodology by identifying the best experiments to improve the effective use of experimental data [2].

The kinetics of $CO_2$ hydrogenation to methanol in a three-phase reactor is used as a case study. The gas phase is continuous, while catalysts (solid phase) are well dispersed in the liquid phase operated in a batch mode. The solvent is selected based on two criteria – low volatility and high methanol solubility. High stirring rate guarantees a fast distribution of components between the gas and the liquid phases. The mathematical model is formulated in ModelBuilder of gPROMS, describing the dynamic behavior of methanol concentration in the liquid phase and carbon species in the gas phase. Graaf’s kinetic model [3] is inserted for the reaction, and the relevant kinetic parameter is explored using the “DoE – experiment execution – parameter estimation” cyclic strategy. The DoE can recommend optimal operational conditions (temperature, pressure, space velocity, sampling time points) for experiment execution, followed by parameter estimation. With several cyclic iterations, an acceptable parameter precision is expected to be achieved with much less effort in the experiment compared to conventional methods.

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# Contents

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