

# A COMPREHENSIVE APPROACH FOR BOTTLENECK IDENTIFICATION IN TRICKLE BED REACTORS FOR THE LIQUID PHASE HYDROGENATION OF VISCOUS AROMATIC DERIVATIVES ON EGG-SHELL CATALYSTS

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## *Abstract*

This contribution offers a methodology to identify bottlenecks in trickle bed reactors for heterogeneously catalyzed liquid phase hydrogenation of viscous aromatic compounds at elevated pressure. In this regard, all necessary steps from laboratory scale reactor design and investigations to the development of a refined reactor model were investigated in a comprehensive approach in a representative case study. The hydrogenation experiments were carried out in a custom-made trickle bed loop reactor, capable of measuring kinetic data free of external mass transfer limitations. For the determination of conversion and selectivity in the experiments, a combination of GC-FID, UV-VIS and NMR was used. The kinetic approach, obtained by these experiments via parameter estimation, was implemented into a 1D+1D (axial and pore domain resolved) reactor-catalyst model for viscous liquids at moderate temperature and high pressure. The equation-based description of the dominating mass transfer influences enables the identification of limitations. As a result, prevailing bottlenecks in pore diffusion could be identified for all components depending on the process conditions.

## *Keywords*

hydrogenation, liquid-phase, multi-phase, catalyst, modelling, heterogeneous catalysis, bottleneck, trickle bed reactor, mass transfer, high-pressure, aromatics, pore diffusion, egg-shell catalyst, parameter estimation.

## **Introduction**

Mass transfer in the liquid phase or between liquid and gas phase often significantly influences liquid phase hydrogenation reactions of aromatic compounds. The design of industrial scale multiphase hydrogenation reactors therefore requires mass transfer considerations. A detailed understanding and an adequate description of the interaction of reaction and mass transport processes is therefore required. This applies particularly to reaction systems of high viscosity, such as substituted aromatic compounds and their respective substituted cycloalkanes,

which in turn feature low diffusion coefficients. To overcome the low solubility of hydrogen in the organic liquid phase, the reaction is performed at elevated pressure of up to 110 bar in the presence of gaseous hydrogen. The aim of this work is the development of a scalable reactor model to describe the complex interaction of heat- and mass transfer and reaction kinetics from micro to macro scale. In this regard, all necessary steps from laboratory scale reactor design and investigations to the

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development of a refined reactor model were investigated within the present study in a comprehensive approach.

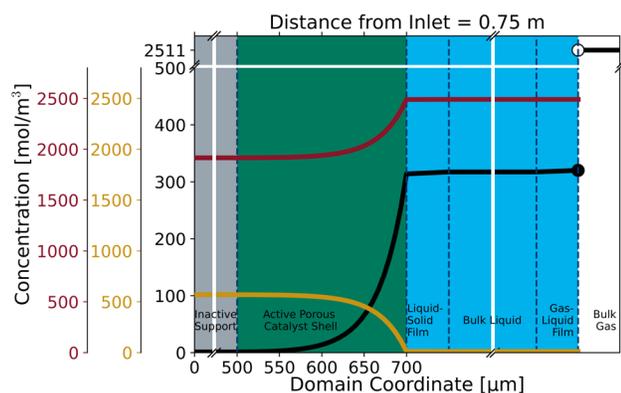


Figure 1. Exemplary radially resolved concentration profiles of the egg-shell particle domain at a fixed axial position. Aromatic species (red), cyclohexane species (yellow) and hydrogen (black).

### Trickle-Bed Loop Reactor: A Reactor Concept for Kinetic Measurements of Heterogeneously Catalyzed Liquid Phase Hydrogenation Reactions

To handle the challenging trickle-flow a special laboratory scale reactor was set up. To ensure a homogeneous liquid distribution in catalytic packed beds as well as for measuring kinetic data unbiased of external mass transfer influences, high liquid superficial velocities are advantageous. Therefore, the well-known trickle-bed reactor concept was modified by implementation of a liquid recycle. The reactor has a low per pass conversion and therefore can be described with model equations for an ideal stirred tank reactor. For the determination of conversion and selectivity in the experiments, a combination of GC-FID, UV-VIS and NMR was applied.

Under process conditions, the plant was used for checking the influence of the external mass transfer resistance by variation of the liquid volume flow. External resistances were proven to be negligible. As next step in the comprehensive study, egg-shell catalysts of different impregnation depth and different active metal loading were investigated. A short-cut method was applied on the resulting experimental data to determine the activation energy of the main reaction. Comparison of the calculated activation energies for each of the catalysts gives an indication on the influence of internal diffusion in the porous catalyst system. One catalyst was identified to show the smallest influence by pore diffusion and was then used in further studies to develop a LHHW-type reaction kinetic approach.

### Advances in Modelling of a Trickle-Bed Reactor for Liquid Phase Hydrogenation Reactions Influenced by Mass Transfer

To describe multiphase reactors the application of pseudo-homogeneous models reduce complexity and computation time and are therefore most often applied. The challenge is to find appropriate correlations that are suited for the application at hand and for the implementation into the reactor model. So far, only few studies have focused on the development of correlations for applications at high pressure, high temperatures and viscous organic compounds.

This knowledge deficit is the motivation for our present work. We contribute to the development of a 1D (axially resolved) model for viscous liquids at moderate temperature and high pressure for the identification and an equation-based description of the most dominating mass transfer influences. In this model, a homogeneous bulk gas phase domain, a homogeneous liquid film domain and a radially resolved particle domain are considered, based on the works of Toppinen et al. (1996) and Julcour et al. (2002). The kinetic approach developed in this work was then implemented in this model.

The results substantiate the assumption of pore diffusion influence on the catalytic system. Dominant bottlenecks in pore diffusion could be identified for all components depending on the process conditions. This is in contrast to the referenced studies at low pressure for components of lower molecular mass, where a dominating limitation solely by hydrogen mass transfer was observed. The applied method as well as the developed model can readily be adapted and applied to other high pressure hydrogenation reactions to identify bottlenecks in mass transfer, thereby indicating opportunities for process intensification in trickle bed reactors.

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