

Simulation of HDS Tests in Trickle-Bed Reactor

V. Tukač¹, A. Prokešová¹, J. Hanika¹, M. Zbuzek² and R. Černý²

¹*Institute of Chemical Technology, Prague, Technická 5, CZ-16628 Prague, Czech Republic*

²*Research and education centre UniCRE Litvínov, CZ-43670 Litvínov, Czech Republic*

Keywords: Hydrodesulfurization Simulation, Catalyst Tests, Trickle-Bed Reactor.

Abstract: The paper deals with methodology of simulation study devoted to evaluation of reliability of HDS catalyst testing procedure in pilot three phase fixed bed reactor. Hydrodynamic behaviour of test reactor was determined by residence time distribution method. Residence time and Peclet number of axial dispersion of liquid phase were obtained by nonlinear regression of experimental data. Hydrodesulfurization reaction kinetics was evaluated by analysis of concentration data measured in high pressure trickle-bed reactor and autoclave. Simulation of reaction courses were carried out both by pseudohomogeneous model of ODE in Matlab and heterogeneous reactor model of PDE solved by COMSOL Multiphysics. Final results confirm presumption of eliminating influence of hydrodynamics on reaction kinetic results by dilution of catalyst bed by inert fine particles.

1 INTRODUCTION

Sustainable development demands ultra-low concentrations of sulfur and nitrogen compounds in produced engine fuels – gasoline and diesel. Present sulfur content valid in EU 10 ppm represents less than one thousands of sulfur content of original crude oil. Deep hydrodesulfurization (HDS) of engine fuels is dominantly carried out in catalytic trickle-bed reactors. Also testing of catalysts affectivity and life cycle needs expensive long time experimentation in pilot scale reactors to evaluate catalyst decay and activity losses. Pilot trickle-bed reactor for catalyst tests needs to produce reliable results not affected by mass and heat resistance. To avoid occurrence of temperature gradients, poor catalyst wetting and fluid maldistribution a dilution of bed of industry scale catalyst particles by fine inert grains is used (Bej et al., 2001). In contradiction to full scale reactors this dilution changes interfacial area in the bed and affects namely external mass transfer of hydrogen (Tukač et al., 2007). Also hydrodynamics, pressure drop, gas and liquid holdups and fluid axial dispersion seems to be quite different (Mary et al., 2009).

The goal of this study was to compare experimental HDS catalyst activity measurement carried out in pilot scale trickle-bed reactor with result of computational model. Catalyst activity tests

were supplemented by kinetic measurement of reaction rate constants and activation energies of selected sulfuric compounds. Parallel to HDS reaction also hydrodenitrogenation (HDN) takes place in the catalytic reactor. Hydrodynamic data were evaluated by residence time distribution (RTD) method in laboratory glass model of pilot reactor. Mathematical models of the process (Ancheyta, 2011) were formulated both like 1D pseudohomogeneous and 3D heterogeneous ones. The aim of this work was generally to evaluate extent of dilution influence on operation of pilot test reactor and to forecast interaction between intrinsic reaction kinetic, hydrodynamic parameters and mass transfer.

2 EXPERIMENTAL

Pilot catalyst activity tests were carried out in high pressure trickle-bed reactor of 30 mm I.D and 887 mm length. In the axis of the reactor 9 mm O.D. temperature probe was located. Reactor bed consists of three section of different porosity, from the top to the bottom: 765 mm calming section of 1-2 mm grain inert, which was followed by two section (110 and 172 mm) of commercial catalyst diluted by different amount (2:1 and 1:1, resp.) of inert. Catalyst particles were in form of trilobe alumina

extrudes of 1.3 mm O.D. and 6 mm mean length and silicon carbide of grain diameter 0.1 - 0.2 mm was used as inert diluent. Scheme of pilot reactor is presented in Figure 1.

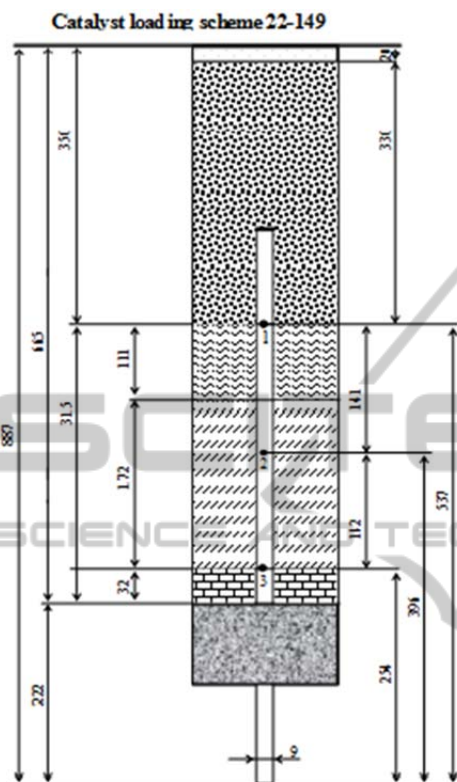


Figure 1: Scheme of pilot trickle-bed reactor with packing layers from top to bottom: silica wool, coarse SiC, diluted catalyst by fine SiC 1:2, diluted catalyst by fine SiC 1:1, coarse SiC, silica wool.

Middle distillates, petroleum fractions for diesel fuel – atmospheric gas oil (AGO) and light cycle oil (LCO) were chosen for catalyst activity tests, their main properties are presented in Table 1. Results of hydrodesulfurization tests carried out with these oils were available to evaluate kinetic parameters, example see in Figure 2.

Kinetic experiments with chosen typical sulfuric substances were carried out in 500 mL stainless steel autoclave equipped by catalyst basket to test activity of industrial shaped hydrodesulfurization catalysts. Both different temperature and hydrogen partial pressure were applied to evaluate kinetic parameters - rate constant and activation energy.

Chemical analysis of content of sulfuric compounds in raw liquid feed and product was made by ASTM standard methods.

Laboratory hydrodynamics test column having identical geometry with pilot reactor consist of glass tube, equipped by three conductivity electrodes with axially located joint ground, which was represented by temperature probe located in axis of tube. Residence time distribution (RTD) method and piston-dispersion (PD) hydrodynamic model were used. Signal responses to impulse injection of concentrated aqueous solution of potassium chloride were measured by three conduct-meters connected with fast multichannel data acquisition system. Air ($7.10^{-4} - 42.10^{-4} \text{ kg m}^{-2} \text{ s}^{-1}$) and water ($0.02 - 0.12 \text{ kg m}^{-2} \text{ s}^{-1}$) feed rate was controlled by mass flow meters on the same values of mass superficial velocities as in the case when diesel fuel and hydrogen were applied. Hydrodynamic parameters (residence time, liquid holdup and Peclet number of axial dispersion) were obtained both by moment method of response curves and nonlinear fitting by numerical simplex method.

Typical properties of raw feed liquid are presented in Table 1. While, AGO exhibits two times greater sulfur content compared to LCO, the last one contains much greater concentration of nitrogen compounds responsible for transient catalyst deactivation.

Table 1: Properties of middle distillates.

Feedstock		AGO	LCO
Density, 15 °C	kg/m ³	857.1	968.6
Refractive index, 20 °C		1.4763	1.563
Color		0.9	2.8
Sulfur content	mg/kg	12900	6346
Nitrogen content	mg/kg	201	750

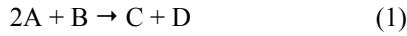
3 PROCESS SIMULATION

Evaluation of experimental data and process simulation are divided to several sections: i) evaluation of kinetic parameters of chemical reactions by nonlinear simplex method, ii) linear regression of catalyst deactivation kinetics, iii) fitting of RTD data to find parameters of PD hydrodynamic model, and finally, iv) formulation of heterogeneous reactor model.

3.1 Reaction Kinetics

In the porous bed, a reaction takes place (Bellos and Papayannakos, 2003) that consumes species A and B and produces C and D, where A, B, C, D represent hydrogen, dibenzothiophene, sulphane, and

biphenyle, respectively in case of sulfur compounds and hydrogen, carbazole, ammonia and biphenyle for nitrogen compounds.



R_i the reaction rate for species i (mol/(m³ s)). Because the reaction takes place in the porous catalytic bed only, the reaction term is zero in the free-flow regions. The reaction rates are given by

$$R_A = -2 k p_A c_B^n \quad (2)$$

$$R_B = R_A/2 \quad (3)$$

$$R_C = -R_B \quad (4)$$

$$R_D = -R_B \quad (5)$$

where k is the reaction rate constant, p_A partial pressure of hydrogen and c molar concentration.

3.2 Pseudohomogeneous Reactors

Pseudohomogeneous plug flow 1D model in Matlab was used to evaluate kinetic parameters of HDS and HDN from the pilot tests. Pseudohomogeneous model represents reactor approximation by ideal piston fluid flow and neglecting of mass and heat transfer limitations. Integrated forms of reactor model for first and other than first reaction order are described by equations 6 and 7, respectively. Parameter $WHSV$ represents weight liquid hourly space velocity. Parameters of the equations were estimated by nonlinear simplex Nelder-Mead fitting procedure.

$$\ln\left(\frac{c_i}{c_{i0}}\right) = -k_i p_{H_2} \left(\frac{1}{WHSV}\right) \quad (6)$$

$$\frac{c_i^{1-n} - c_{i0}^{1-n}}{n-1} = k_i p_{H_2} \left(\frac{1}{WHSV}\right) \quad (7)$$

3.3 Heterogeneous Reactor

CFD 3D model of hydrodynamics in pilot reactor was made in Comsol Multiphysics FEM solver (Zimmerman, 2007). Heterogeneous reactor model incorporates mass and heat transfer limitations. The developed model incorporates of Navier-Stokes momentum balance of fluid flow with Brinkman extension for porous reactor bed. Both chemical kinetic, mass transfer of reactants and heat convection and conduction are taking into account.

3.3.1 Domain Equations - Fluid Flow

The stationary Navier-Stokes equations describe the fluid flow in the free-flow regions. In the porous bed, the Brinkman equations for porous media is applied.

From assumption that the modeled species are present in low concentrations compared to the solvent oil. follows that using of a Fickian approach for the diffusion term in the mass transport is approved. Model involve the mass transport for the four species A, B, C, and D with the convection-diffusion equation

This model shows the flow field in an experimental reactor for studies of heterogeneous catalysis.

$$\begin{aligned} -\nabla \cdot \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p &= 0 \\ \nabla \cdot \mathbf{u} &= 0 \end{aligned} \quad (8)$$

The model couples the free fluid and porous media flow through the Navier-Stokes equations and Brinkman's extension of Darcy's law.

The mass transport of three species in the reactor is modelled through the diffusion and convection equation.

$$\begin{aligned} -\nabla \cdot \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \frac{\eta}{k} \mathbf{u} + \nabla p &= 0 \\ \nabla \cdot \mathbf{u} &= 0 \end{aligned} \quad (9)$$

In the above equations η denotes the viscosity, ρ the density, and k the permeability.

3.3.2 Domain Equations – Mass Transport

The mass transport is given by the diffusion and convection equation:

$$\nabla \cdot (-D_i \nabla c_i + \mathbf{u} c_i) = R_i \quad (10)$$

where c_i denotes the concentration (mol/m³) of species i , \mathbf{u} the velocity vector D_i the diffusivity (m²/s), and R_i the reaction rate (mol/(m³.s)) for species i .

$$1/WHSV, \text{ h.kg}_L/\text{kg}_L$$

3.3.3 Boundary Conditions

A constant velocity profile is assumed at the inlet boundaries:

$$\mathbf{u} = \mathbf{u}_{in} \quad (11)$$

For the outlets, pressure conditions are applied. In the mass transport, the concentrations at the inlet are fixed:

$$c_i = c_{i0, \text{inlet}} \quad (12)$$

At the outlet, assume that convection dominates the mass transport:

$$\mathbf{n} (-D_i \nabla c_i) = 0 \quad (13)$$

This implies that the gradient of c_i in the direction perpendicular to the outlet boundary is negligible. This is a common assumption for tubular reactors with a high degree of transport by convection in the direction of the main reactor axis. The condition eliminates the need for specifying a concentration or a fixed value for the flux at the outlet boundary. At all other boundaries, insulating conditions apply:

$$\mathbf{n} (-D_i \nabla c_i + c_i \mathbf{u}) = 0 \quad (14)$$

4 RESULTS AND DISCUSSION

Following presented results deals with estimated kinetic parameters and catalyst deactivation rate combined with hydrodynamic results obtained by RTD method. The last part represents results of reactor model.

4.1 Kinetic Parameters

Kinetic parameters of equation 2 were evaluated from experiments with different weight liquid hourly space velocity (WHSV). It follows from Figure 2 that reaction order with respect to sulfuric compounds was found 1.37 and first order with respect to nitrogen compounds.

4.2 Catalyst Deactivation

Deactivation of HDS catalyst in course of operation period represents a serious problem. To predict kinetics of deactivation a long time experiments are necessary. Possible way how to accelerate deactivation process is to combine raw liquid feeds, AGO and LCO, respectively, with different content of coke precursors, e.g., aromatics.

Result of this arrangement is possible to see on Figure 3, HDS rate constant course in time on stream (TOS). By periodic setting of standard reaction condition: feed composition and temperature and pressure, data presented in Figure 4

were obtained. Data measured at standard reaction conditions represent decrease of reaction rate in time due to catalyst deactivation. From this Figure 4 deactivation constant for presumed first deactivation order was evaluated by linear regression.

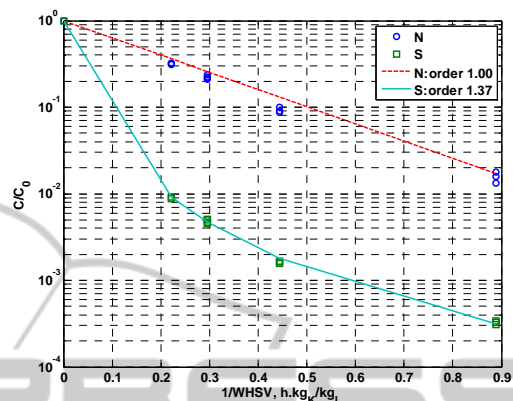


Figure 2: Rate constant and reaction orders with respect to sulfuric and nitrogen compounds.

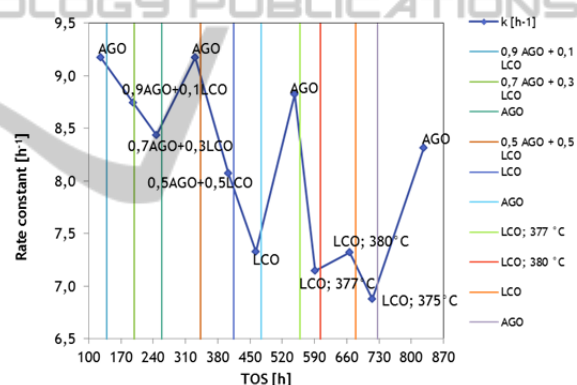


Figure 3: Example of typical accelerated activity test with AGO an LCO feedstock. Operating parameters: pressure 4.5 MPa, Oil feed 1 kg/dm³_{cat.}, hydrogen/liquid feed 300 Nm³/m³.

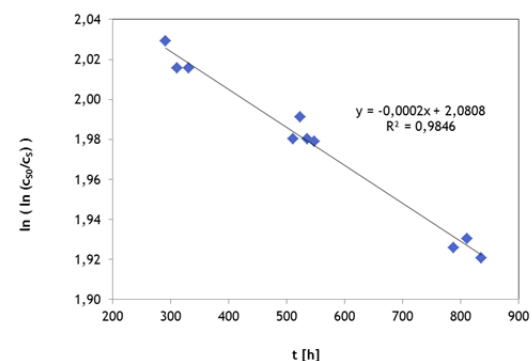


Figure 4: Linear fitting of first order deactivation.

4.3 RTD

To formulate hydrodynamic model of the pilot reactor determination of flow pattern in catalytic bed is necessary. This is possible experimentally by the RTD method. Resulting parameters of piston dispersion (PD) model (Villiermaux and van Swaaij, 1969), ie, Pe number and liquid holdup were evaluated by nonlinear fitting simplex procedure of Equation 15.

$$E(\Theta) = \frac{1}{2} \left(\frac{Pe}{\pi\Theta} \right)^{1/2} \exp\left(-\frac{Pe(1-\Theta)^2}{4\Theta}\right) - \frac{Pe}{2} e^{-Pe} \operatorname{erfc}\left[\frac{(Pe/\Theta)^{1/2}(1+\Theta)}{2}\right] \quad (15)$$

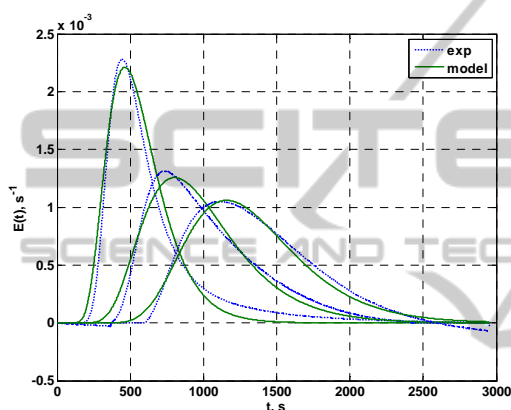


Figure 5: Comparison of PD model with RTD experiment.

E represents tracer distribution function, Θ is dimensionless time, and Pe is Peclet number. Good agreement between PD hydrodynamic model (Equation 15) and experiment is presented in Figure 5.

4.4 CFD Reactor Model

In the Figure 5 the CFD model solution of sulfur concentration field in tested trickle bed reactor is presented. Reactor bed is divided to three zones with different porosity: i) calming zone to reach phase equilibrium and steady state fluid velocity profile, ii) first reaction zone of diluted catalyst and, iii) second reaction zone of diluted catalyst. To evaluate an influence of resulting parabolic velocity profile on sulfur compound concentration is possible. Decreased porosity of diluted catalytic reactor bed exhibit more flat velocity profile, so as more even reactants concentration on bed cross-section. Kinetic Equation 2 of hydrodesulfurization of different compounds, e.g. dibenzothiophene, were incorporated into model to simulate real reactor behavior.

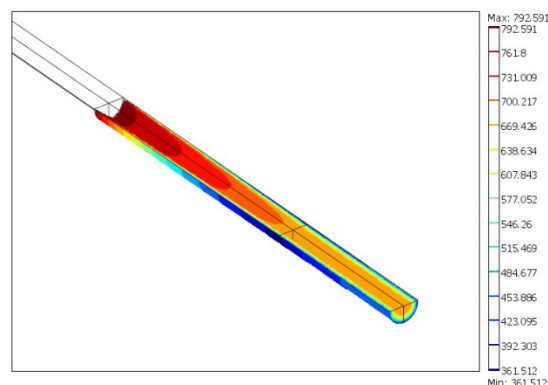


Figure 6: CFD model of pilot reactor with dibenzothiophene concentration field.

5 CONCLUSIONS

To support experimental testing of hydrodesulfurization catalysts in pilot scale trickle-bed reactor a methodology based on process simulation was developed. Time dependent models were used to evaluate both kinetic of HDS and HDN reactions and description of catalyst activity decay based on experiments. Also RTD measurement of liquid holdup and axial dispersion in catalytic bed was evaluated by piston dispersion (PD) hydrodynamic model of time response characteristic. Resulting kinetic parameters, deactivation constant and Peclet number were used to formulate steady state heterogeneous reactor model. Effect of different inert diluent grain size on performance of pilot scale HDS catalytic reactor was successfully evaluated by CFD model. Time dependent kinetic in combination with steady state flow velocity was used to compare with experimental measurements.

ACKNOWLEDGEMENTS

This publication is a result of the project no. FR-TI3/084, supported by the Ministry Industry and Trade, which is being carried out in the UniCRE centre whose infrastructure was supported by the European Regional Development Fund and the state budget of the Czech Republic. Also financial support from specific university research (MSMT CR no. 20/2014) is also acknowledged.

REFERENCES

- Ancheyta, J., 2011. *Modeling and Simulation of Catalytic Reactors for Petroleum Refining*, John Wiley & Sons, Inc. Hoboken, 1st edition.
- Bej, S.K., Dalai, A.K., Maity, S.M., 2001. *Effect of diluent size on the performance of a micro-scale fixed bed multiphase reactor in up flow and down flow modes of operation*. *Catalysis Today* 64, 333-345.
- Bellos, G.D., Papayannakos, N.G., 2003. *The use of a three phase microreactor to investigate HDS kinetics*. *Catalysis Today* 79–80, 349-355.
- Mary, G., Chaouki, J., Luck, F., 2009. *Trickle-bed laboratory reactors for kinetic studies*. *International Journal of Chemical Reactor Engineering* 7 R2, 1-68.
- Tukač, V., Šimičková, M., Chyba, V., Lederer, J., Kolena, J., Hanika, J., Jiříčný, V., Staněk, V., Stavárek P., 2007. *The behavior of pilot trickle-bed reactor under periodic operation*. *Chemical Engineering Science* 62, 4891-4895.
- Villermaux, J., van Swaaij, W.P.M., 1969. *Modèle représentatif de la distribution des temps de séjour dans un réacteur semi-infini à dispersion axiale avec zones stagnantes. Application à l'écoulement ruisselant dans des colonnes d'anneaux Raschig*. *Chemical Engineering Science* 24, 1097-1111.
- Zimmerman, W.B.J., 2007. *Multiphysics Modelling with Finite Element Methods*, World Scientific, Singapore. 2nd edition.