

Activation of Catalysts in Commercial Scale Fixed-Bed Reactors: Dynamic Modelling and Guidelines for Avoiding Undesired Temperature Excursions

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Highlights

- Full dynamic model for activation of catalysts in commercial scale fixed-bed reactors.
- Key dimensionless numbers and practical guidelines for both engineers and chemists.
- Simple peak temperature expressions both for kinetic and mass transfer controlled regime.
- Counter intuitive effects elucidated.

1. Introduction

It is not widely recognized that during the activation of heterogeneous catalysts in commercial scale (near) adiabatic fixed bed reactors, the interaction of heat propagation and exothermic reactions may give rise to local temperature excursions beyond the adiabatic temperature rise. This is particularly significant for gas phase activation due to the large ratio of heat capacities of the stagnant solid phase and flowing gas phase. Excessively high catalyst temperatures can cause significant deterioration of catalysts and operational problems. The goal of this work is to develop simplified criteria as guidelines for avoiding or minimizing undesired temperature excursions. This study builds upon dynamic modelling work reported by Westerterp *et al.* on decoking of catalysts [1], adapting to generic gas-solid reactions in fixed bed reactors.

2. Methods

In that earlier decoking study [1] where a full dynamic model was developed using worst-case scenario assumptions, it was found that the moving reaction and heat fronts form an accumulation zone and the catalyst temperature reaches a pseudo-steady state plateau under most operating conditions. We have subsequently implemented the above model in gPROMS and transformed the kinetics into a generic catalyst reduction/oxidation case with arbitrary stoichiometry: $aA(g) + bB(s) \rightarrow cC(g) + dD(s)$. The following key assumptions made by Westerterp *et al.* were made initially too and then relaxed:

- 1) constant gas density and gas velocity,
- 2) negligible net transfer of mass between gas and solid phase,
- 3) negligible heat losses to the surroundings (or coolant for a multi-tubular reactor)
- 4) gas-solid reaction fully controlled by external mass transfer.

This analysis enabled the derivation of simple expressions for heat front and reaction front velocities, plateau temperature and the solid phase overheating. The sensitivity of these parameters was investigated by removing/relaxing one assumption at a time and incorporating data for the reduction of copper(II) oxide with hydrogen and copper oxidation with diluted air as examples.

3. Results and discussion

Simplified approximations for the velocities of the heat front u_{hf} and reaction front u_{rf} were derived:

$$u_{hf} \approx \frac{u_0(\rho C_p)_{G0}}{(1-\varepsilon)(\rho C_p)_S}, u_{rf} \approx \frac{b}{a} \frac{u_0 C_{A0}}{(1-\varepsilon)\rho_S C_{B0}}, \gamma = \frac{u_{hf}}{u_{rf}} \approx \frac{a}{b} \frac{C_{P,G}}{C_{P,S}} \frac{M_G}{M_B} \frac{L_B}{x_{A0}} \quad (1)$$

L_B and x_{A0} being the metal loading (wt%) on the catalyst and the molar fraction of H_2 or O_2 (vol%), respectively. Depending on the Lewis number, the maximum temperature rise of the catalyst (defined as rise over the inlet

temperature) can be predicted very well by Eq. (2). The results confirm that as per Eq. (2), for a given value of γ (< 2), the temperature rise in the bed exceeds the adiabatic temperature rise. Results reveal critical H_2 or O_2 concentrations at which the temperature never reaches a pseudo-steady state ($\gamma \approx 1$). Moreover, for a certain range of conditions a decrease in concentration can lead to an *increase* of the temperature rise.

$$\Delta T_{max} = \frac{\Delta T_{ad}}{|\gamma - 1|} \text{ for } Le \geq 1; \quad \Delta T_{max} = \frac{\Delta T_{ad}}{\gamma - 1} \cdot \frac{\gamma}{1 + (\gamma - 1)Le^{2/3}} \text{ for } Le < 1 \text{ and } \gamma > 1 \quad (2)$$

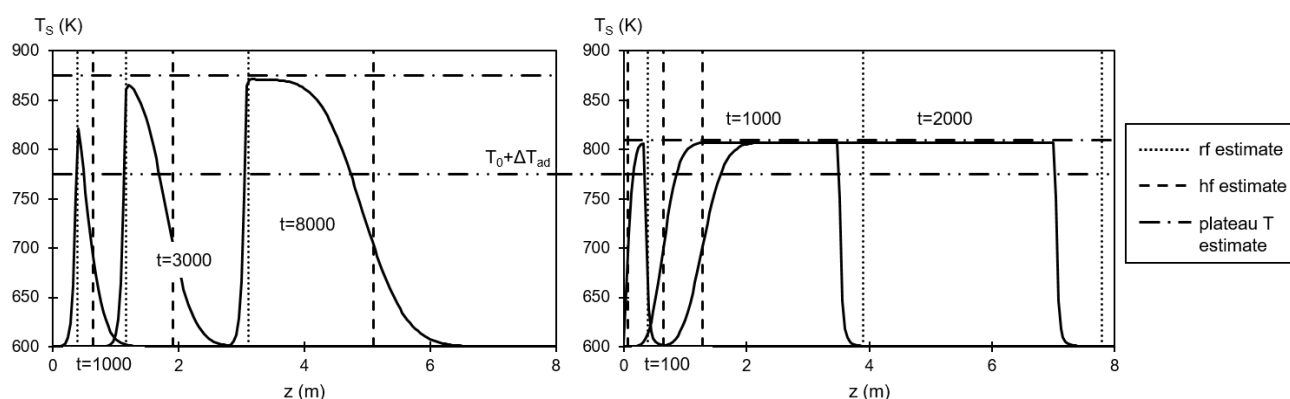


Figure 1. Reduction of 15wt% Cu catalyst. Solid temperature profile of full dynamic model without assumptions (1) and (2)
Figure 1-a (left): 2% vol O_2 in N_2 , $\gamma = 1.64$; Figure 1-b (right): 20% vol O_2 in N_2 (Air), $\gamma = 0.164$;

Remarkably, relaxing assumption 1) the simplified expressions Eqns (1-2) remain very accurate in predicting the position of fronts and plateau temperature in modelling results although gas density and velocity change significantly with gas temperature (up to a factor 2 or more). Similarly, after also relaxing assumption 2), the mass flow rate changes significantly (i.e. H_2 to H_2O) but Eqns (1-2) remain remarkably accurate, see Fig. 1.

For the relaxation of assumption 3), i.e. with heat loss implemented, up to losses representative of a wall cooled multi-tubular reactor, modelling results show that the plateau feature no longer exists. However, it was found that ΔT_{max} decreased only to a remarkably limited extent, especially for cases of $\gamma \ll 1$. The temperature at critical H_2 or O_2 concentrations was observed to reach a constant peak value. Finally, relaxing assumption 4), for reasonably fast kinetics, the plateau feature of the temperature profile develops over a longer time and further down the reactor but again the prediction for ΔT_{max} by Eq. (2) remains useful.

4. Conclusions

Maximum temperature rise estimations have been derived for the assessment of catalyst activation processes. Rigorous modelling shows that these estimations are remarkably robust and accurate, even for models without the simplifying assumptions 1) to 4). While deviations at low H_2 or O_2 concentrations ($\gamma \gg 1$) can be significant with heat loss and reaction kinetics, the temperature approximation remains relevant as a maximum permissible temperature. Hence the simple eqns (1-2) provide easy to use guidelines for predicting and preventing undesired temperature rises during activation of catalysts in general, i.e. not only for severe cases mentioned in the introduction where the excursions can go well beyond the adiabatic temperature rise.

References

- [1] Westerterp, K.R., Fontein, H.J. and van Beckum, F.P.H. (1988). Decoking of Fixed Bed Catalytic Reactors. Chemical Engineering & Technology – CET, 11(1), pp. 367-375.

Keywords

Catalyst activation; Overheating; Dynamic modelling; Temperature excursions