Simulating Catalyst Deactivation in Ethylbenzene Dehydrogenation

Matthias Feigel[1*], Johanna Fernengel[1], Michael Balakos[2], Yuma Kuraguchi[3], Nobuaki Kodakari[3]

[1]*Clariant Produkte (Deutschland) GmbH, Arabellastr. 4a, 81925 Munich, Germany*
[2]*Clariant Corporation USA*
[3]*Clariant Catalysts (Japan)*

**matthias.feigel@clariant.com*

Highlights

- Deactivation model to predict the activity loss in ethylbenzene dehydrogenation.
- Radial temperature profiles allowing better understanding of the current catalyst activity.
- Accurate predictions of end of runs and projections of the current run can be done.

1. Introduction

Ethylbenzene (EB) dehydrogenation is an important industrial process that produces styrene monomer. It involves the catalytic dehydrogenation of ethylbenzene over an iron oxide-based catalyst. The reaction is endothermic and operates at high temperatures around 600-650°C with steam as a diluent and heat providing agent. The pressure is kept low to drive reaction toward the product styrene. As such, the plethora of industrial applications use radial reactors due to their low pressure drop.
A major challenge in EB dehydrogenation is catalyst deactivation over time due to different mechanisms [1]. The two major considered deactivation mechanisms comprise coke deposition and the loss of potassium, which is a commonly used promoter in EB catalysts [2]. The buildup of carbonaceous deposits on the catalyst surface is regulated by the steam-to-hydrocarbon ratio (SHR) in some extent. However, the loss of potassium is irreversible and thus, the catalyst decreases in activity over time. This causes the temperature profile within the reactors to change from the start of the run towards the end of run as the activity declines. To counter the activity loss, the temperature at the reactor inlet is increased over time until a maximum tolerable temperature is reached which is related to metallurgical limits. Additionally, the formation of side products is enhanced.
Explicitly modeling this deactivation behavior and kinetics is crucial for accurately predicting reactor temperature profiles and catalyst lifetime. By incorporating deactivation functions into our process modeling software, the gradual activity loss and resulting temperature changes can be captured.

2. Methods

Kinetic data were collected from a pilot-scale ethylbenzene dehydrogenation unit over a 6-month experimental campaign. The unit contains two axial flow reactors equipped with external heaters and CLN´s latest generation iron oxide-based commercial EB dehydrogenation catalyst. Different operating conditions were evaluated, spanning a range of temperatures (580 – 650°C), SHR ratios (6 – 9), pressures (0.3 – 1 bar) and LHSVs (0.3 – 0.6 h^{-1}). Compositions of the reactor inlet and outlet streams were measured using online gas chromatographs, while temperatures were recorded by thermocouples inserted within the catalytic bed at various axial positions.
The extensive pilot plant data was used to develop a rigorous simulation model incorporating kinetic expressions, heat and mass balances, and deactivation functions to predict performance over the lifespan of the EB dehydrogenation catalyst. The deactivation model was validated with available plant data. Modeling was performed with gPROMS.

3. Results and discussion

Figure 1 illustrates two characteristic temperature profiles typically encountered in industrial operation, which are simulated by the model. At the start of run, the temperature drops over the radial domain, as expected for an endothermic reaction. The activity of catalyst is at its initial state. Approaching the end

of run, the catalyst is already deactivated in the beginning section of the bed. Throughout operation, a deactivation front progresses through the bed with a sigmoidal shape. As the catalyst slowly deactivates, the rate of reaction is diminished and therefore, no drop in temperature can be observed. The plateau is an indication of the deactivated region of the bed. Even though, half of the bed is reached in the case of Figure 1, only 25% of the bed is deactivated.

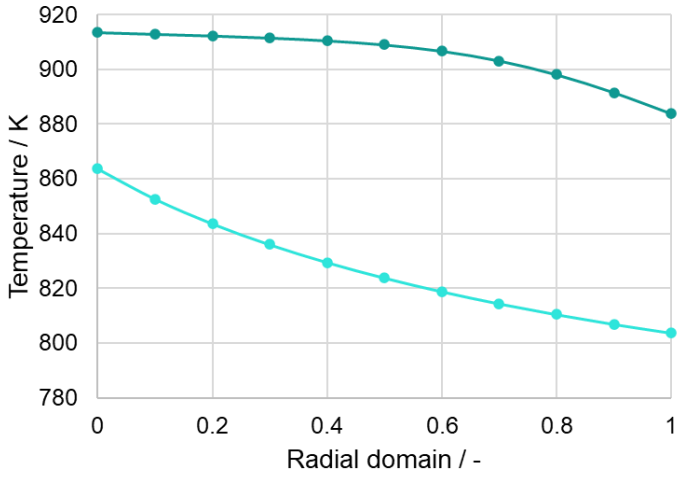

Figure 1. Temperature profile over radial domain at start of run and towards end of run.

4. Conclusions

In this work, a comprehensive kinetics-based model was developed to capture catalyst deactivation and temperature profile changes in ethylbenzene dehydrogenation in industrial application. Rigorous modeling of gradual activity loss was achieved by incorporating an innovative approach to simulate deactivation behavior. The key benefit of the distributed model is to give local information about the activity of the catalyst instead of aggregated information. The validated model demonstrated excellent accuracy in predicting temperature rises and conversion declines over catalyst lifetimes. Overall, this advanced simulation methodology delivers deeper understanding of commercial EB dehydrogenation operation and aids optimization across process reliability, productivity, and economics. The techniques are broadly applicable to other catalyzed processes facing progressive catalyst decay.

References

[1] G. R. Meima, P. G. Menon, Appl. Catal., A 212 (2001), 239–245
[2] I. Rossetti, E. Bencini, L. Trentini, L. Forni, Appl. Catal., A 292 (2005), 118–123

Keywords
Process modeling; ethylbenzene dehydrogenation; deactivation; radial reactors