

CATALYST DEACTIVATION IN 3D CFD RESOLVED PARTICLE SIMULATIONS OF PROPANE DEHYDROGENATION

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Summary

Catalyst deactivation by carbon deposition has been investigated for the catalytic propane dehydrogenation reaction using computational fluid dynamics to couple the transport and reaction processes occurring inside the cylindrical pellet to the gas flow of reactants in the bed. The pellet scale reaction and carbon laydown are shown to be strongly affected by the bed scale tube wall heat flux supplied for the endothermic reactions, and the species distributions on the pellet surface are affected by the ease or otherwise of reactant access to the particle.

Keywords

Hydrogen production, dynamics of chemical reacting systems, multiscale analysis

Introduction

The deactivation of catalysts is an important problem in many processes, such as steam reforming and the catalytic dehydrogenation of alkanes, which feature highly endothermic reactions. The local carbon laydown can cause particle breakage or strongly decrease reaction rates, both of which remove the heat sink and lead to local hot spots and reactor tube failure. This is especially a problem for reactors with a low tube-to-particle diameter ratio (N), where a large fraction of the catalyst particles are located next to the heated tube wall.

We want to understand pellet deactivation on the local or microscale level, and how the intraparticle deposition of carbon interacts with the gas-phase fluid flow around the particle. The application of detailed computational fluid dynamics (CFD) to packed tubes has been recently reviewed¹ and our previous work² has introduced the coupling of gas flow to resolved species and temperature gradients inside pellets by CFD for steam reforming, without considering deactivation. The objective of this work is to use CFD to examine the interaction between flow and reaction/deactivation for the case of propane dehydrogenation (PDH) to propene, for which kinetics of reaction and deactivation are available.³ This is an important commercial reaction, due to the world demand for propene monomer for polypropylene manufacture.

Method

CFD simulations of flow, heat transfer, diffusion and reaction were carried out using the commercial CFD code Fluent 6.3 in a 3D 120° periodic wall segment of an $N=4$

tube, as shown in Fig. 1. Focus is on a central full cylinder test particle at a 45° angle to flow, in realistic surroundings of particle segments. The mesh consisted of boundary layer prism cells at both the inside and outside particle surfaces and at the tube wall, with tetrahedral cells in the main fluid volume. The unstructured mesh cell size was 7.6×10^{-4} m with a total cell count of 1.5 M cells.

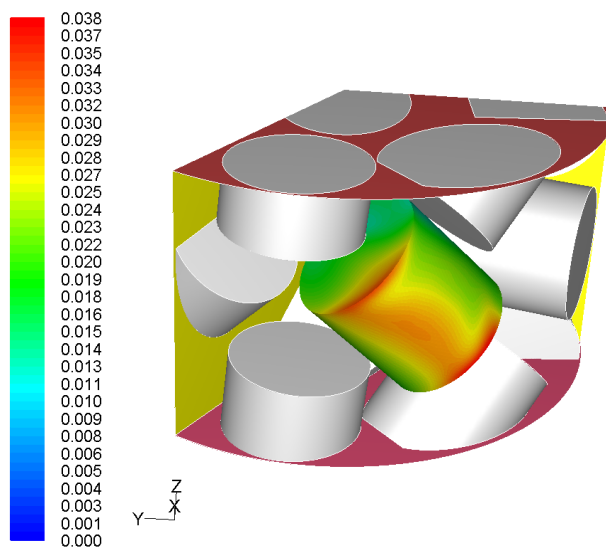
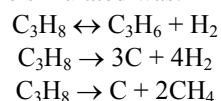


Figure 1: Propane dehydrogenation reaction rate contours ($\text{kmol/m}^3(\text{solid})\cdot\text{s}$) on test particle in 120° wall segment

The reaction scheme simulated was:



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These reactions were represented in the solid particles using user-defined scalars to mimic species transport and reaction, with user-defined functions supplying reaction rates. Diffusion in the particles was modeled by Fick's law using an effective diffusivity, given by Hite and Jackson's approximation of the Dusty Gas Model (DGM).⁴

Results and Discussion

Results are shown below for inlet PDH conditions of 600 °C and 1 atm, with pure propane feed. The wall heat flux was chosen to keep the gas temperature change close to zero. The distribution of the main propane to propene reaction on the surface of the test particle is shown in Fig. 1. The reaction rate follows the temperature very closely, and both are highest closest to the tube wall. Product mass fractions are shown in Fig. 2 on an "unrolled" curved surface of the test particle, and are not highest in the same location due to the accessibility of flow bringing fresh reactants and removing product species.

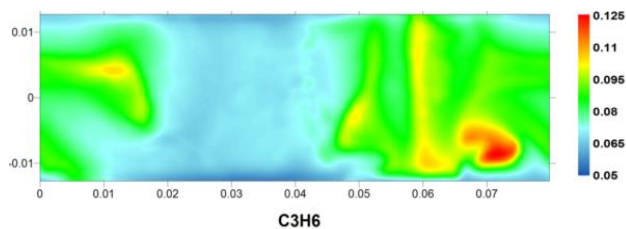


Figure 2: Mass fraction of propene (C_3H_6) on the surface of the test particle

New results shown here are the particle surface map of carbon production rate shown in Fig. 3. Here, the highest carbon production rate occurs where the temperature and the carbon-deposition reaction rates are highest. This map shows that carbon deposition is quite asymmetrical in the pellet, which can lead to uneven rates of thermal expansion and contraction, which have the potential to break the particle, or to cause local hot-spots due to the deactivation of the endothermic reaction heat sinks.

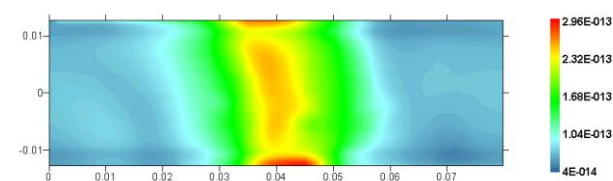


Figure 3: Carbon production rate (kg/s) on the surface of the test particle

Inside the particles, the time evolution of the carbon deposits can be tracked by running the CFD simulation at base case (undeactivated) conditions to obtain local carbon deposition rates, then accumulating these over a 60-second interval to obtain the local carbon build-up C_C . This is then inserted into the deactivation rate expression:

$$R_i = R_{i0} \exp(-\alpha C_C)$$

which is used to modify the reaction rates with fresh catalyst R_{i0} to give the reaction rates after 60 s. The CFD simulation is then run for a further 60-second time period to obtain increased values of C_C and the process repeated. The results for a series of four times are shown in Fig. 4. Within a near-wall particle the carbon first develops in the pellet near the tube wall, with a carbon gradient inside the pellet. A higher layer of carbon is shown near the tube surface, suggesting that "shrinking-core" behavior would be observed at longer times.

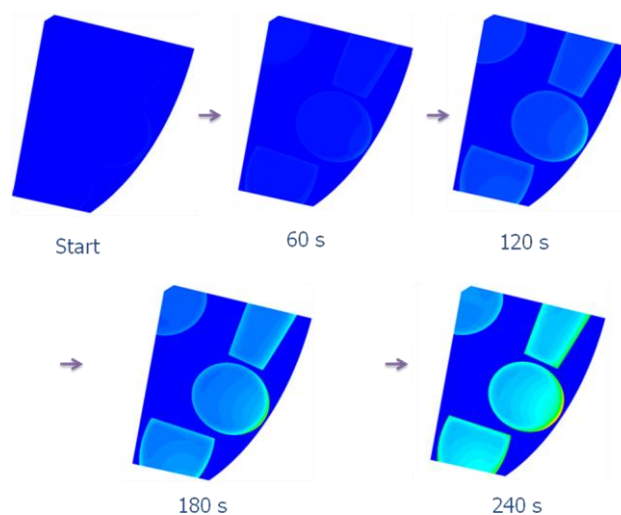


Figure 4: Time evolution of carbon laydown inside near-wall catalyst particles

Conclusions

Computational fluid dynamics methods have been extended to show local details of carbon laydown both on the surface of, and inside near-wall catalyst particles. The distribution of carbon is affected by the wall heat flux and resulting near-wall high temperatures, and the flow around the particle in constricted areas. Future work will relate this information to the design of catalyst particles.

References

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