

DEVELOPMENT OF AN EULERIAN SOLVER FOR FLUIDIZED BEDS UNDER DEACTIVATION CONDITIONS

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1 INTRODUCTION

Catalytic reactions are widely spread throughout the chemical industry, taking part in key processes in the production of chemicals, feed-stock and plastics. Catalyst deactivation plays a major role in the overall process efficiency and its correct modeling and prediction in industrial scale reactors is becoming increasingly important. This problem has already been tackled through the use of numerical methods (Cordero-Lanzac et al. 2020) in a simplified lump approach of a paradigmatic model reaction, such as methanol to olefins (MTO). This approach based on tracking catalyst deactivation is limited for fluidized beds, as heterogeneous void fraction profiles considerably affect mixing, reaction and the resulting deactivation of the catalyst. Thus, the coupling of the deactivation model within the computational fluid dynamic (CFD) framework is proposed in order to alleviate some of the previously mentioned limitations.

2 METHODOLOGY

OpenFOAM(v1912) allows for the simulation of such systems through the *reactingTwoPhaseEulerFoam* solver. An Eulerian-Eulerian approach is taken for the multiphasic system and the solid-solid collisions and bed packing are modeled by the kinetic theory of granular flows (KTGF). This approach enables the simulation of reactive systems in gas phase, which in turn is filtered by a partially stirred reactor turbulent model (PaSR). Catalytic gas-solid systems are affected by the hydrodynamics and heat transfer of non-reactive fluidized beds, apart from the volumetric solid content and distribution, and catalytic activity of the bed, according to

$$-\frac{dx_{j,i}}{dt} = \varepsilon_s \theta_i a_i A_o e^{\frac{-Ea}{RT_i}} \prod_{j=1}^n x_{j,i}^l$$
(1)

where $x_{j,i}$ is the molar fraction of *j* compound in cell *i*, ε_s is the solid volume fraction, θ_i inhibition constant of water in the reaction, a_i is the catalyst activity, A_o is the Arrhenius pre-exponential constant and Ea is the activation energy.

The addition of these properties, requires the partial implementation of the gas and solid model from the

basic components shown in Figure 1. The solid phase (*catalyticPhase*) requires an activity scalar field defined by its transport equation. The type of source-sink term of this equation is selected at run-time between the models already implemented.



Figure 1. Simplified UML diagram of the catalytic phase system implementation in CFD.

In some catalytic processes, the catalyst only gets deactivated with time due to a clogging of the pores by the reaction by-products, which requires for the deactivation function to only depend on temperature, with a simple kinetic expression as follows

$$-\frac{d a_i}{dt} = A_d e^{\frac{-E_d}{RT_i}}$$
(2)

However, in some processes the mere presence of some components in the gas phase initiates and accelerates said deactivation on the catalyst. Thus, a phase model derived form the base phase model class is developed, where a list of pointers are kept, tracking the gas phase component fields that the user selects following Equation 2, note that the activity term could be positive in case a catalyst regeneration process in underway.

$$-\frac{da_i}{dt} = A_d e^{\frac{-E_d}{RT_i}} \sum_{j=1}^n \left(x_{j,i} \right) a^k$$
(3)

where $x_{i,j}$ is molar fraction of the component involved in the catalyst deactivation in cell *i*, *k* is the deactivation order, A_d is the deactivation pre-exponential contact and E_d is the deactivation activation energy.

The final activity source term in Equation 2 is implemented in a semi-implicit fashion, in order to increase the numerical stability of the case. However, numerical stability is not particularly a problem in the current deactivation case as high deactivation rates incur in lower reaction source terms, and hence it is self stabilized. On the other hand, solution boundedness is required and not guarantied by the transport equation itself. This requirement is specially important for the lower limit, as negative activities induce virtual sources in arbitrary locations. Thus, a van Leer discretization scheme (van Leer 1979) is used in addition to an explicit truncation operation after the transport equation has been solved.

In addition, the reaction source terms in a catalytic reaction do depend in the amount of catalyst that is present in a volume, which requires the gas phase reaction term to be linked with the solid void fraction value. This is attained by looking into all phase pairs and selecting the newly created *catalyticPhaseModel* at run time, in case multiple catalyst phases are present, in the current implementation, their void fraction contribution are added to the total catalyst content. By following this approach, fluidized beds with significant gas bubble sizes in the bed will not have a constant reaction rate for the whole bubble, but rather a maximum reaction rate at the edges of each bubble as the bulk of the continuous phase does not contribute as much to the overall yield of products.

3 RESULTS

The MTO conversion in a fluidized bed is run for 30 min (simulation time) with the kinetic and deactivation constants given by Cordero-Lanzac et al. (2020). Figure 2(a) shows a gas void fraction cross section with a stable fluidization and reasonably good gas-solid contact. The good mixing of the catalyst leads to a homogeneous activity value. It is worth noting certain activity is present above the freeboard (>0.5 m) as big bubbles eject particles above the freeboard, thereby transporting the scalar. The axial activity profiles get progressively reduced as times goes on, as shown in Figure 2(b), in which 50% drop in activity across the whole bed is observed after 10 min on stream. This model allows calculating the evolution of each product and, furthermore it is able to resolve more complex geometries and configurations, such as when there is a net flow of catalyst.



Figure 2. Test case (a) cross section void fraction field and (b) axial activity evolution

The model allows to use the kinetic constants obtained by the fitting of chemical kinetic studies and account for the deactivation that takes place in a fluidized bed, which allows to study the effect of the hydrodynamics and solid-gas mixing in the overall deactivation of the bed inventory.

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