Generalized Runaway Diagrams for Catalytic Reactors with Stacked Catalyst Activities.

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Highlights

- Extended Barkelew type diagrams to non-uniform catalyst activity
- Exploited newly found behavior of loci of the two hot spot inflection points
- Both hot spots equally limiting as guidance for optimization.

1. Introduction

The theory for thermal stability in wall cooled catalytic multi-tubular reactors is well known in cases where there is a single catalyst activity in the tubes, see for example the pioneering work done by Dente and Collina [1], Barkelew [2] and Van Welsenaere and Froment [3]. In the last two decades it has been identified that for a number of specific applications it can be beneficial to apply stacking of catalysts with different activities. For a uniform catalyst activity, the productivity of the whole bed is typically limited by the parametric sensitivity around the location of the hot spot. By deliberately lowering the activity in the region of this hot spot and simultaneously increasing the activity in the downstream part, one can expect an overall increase in maximum productivity, or Space Time Yield (STY). As a consequence of the higher activity in the bottom part, a second hot spot may develop. In terms of runaway diagrams this then would translate into a shift in the runaway boundary, decreasing the region of "runaway" or "parametric sensitivity". There have been a few case studies published, but to the best of our knowledge there has not been any attempt to extend or generalize the classic work to the case of two (or more) catalyst activities. In applications specific to Shell we had confirmed experimentally that indeed stacking of catalyst activity can increase the maximum STY for an existing reactor. However, the observed advantages were relatively limited. The question arises whether this is due to the specifics of the applications studied, or points to a more general conclusion.

In this work we have made a first attempt to develop modified runaway diagrams for the general case of two activities, stacked on top of each other. The degrees of freedom are 1) the activity ratio A_2/A_1 with the constraint of constant total activity and 2) the dimensionless step-change location *S*, the start of the second catalyst. Our goal is to use these modified diagrams as a quick screening tool to assess for any application whether stacking of catalyst activity has potential to significantly increase the STY.

2. Methods

We largely used the reactor model assumptions and equations and as previous authors had done in developing the classic runaway diagrams for uniform activity. For the definition of "runaway" we used the classic, albeit still somewhat arbitrary, onset of an inflection point in the dimensionless axial temperature profile. There now can be two relevant inflection points: either before the first hot spot or before the second hot spot, hence we developed a numerical algorithm to detect this. Starting from the uniform activity case we systematically varied the two degrees of freedom for the activity profile, i.e. A_2/A_1 and *S* under the constraint $A_1S + A_2(1 - S) = 1$. For each of the parameter values the runaway loci were plotted in a modified Barkelew diagram with y-axis the inverse of the Semenov number ψ and on the x-axis the dimensionless product of the adiabatic temperature rise and activation energy, *B*. For any stacking configuration the vertical "distance" to the runaway boundary of the stacked catalyst from that of A_2/A_1=1 or *S*=1 (viz. uniform activity) is indicative for the potential magnitude of improvement.

3. Results and discussion

Figure 1-a shows in a Barkelew type diagram the loci of the inflection points for *S*=0.25 and A_2/A_1=1.60 as well as for the uniform activity case. For each of the 6 regions (a-f) a typical axial temperature profile

is also shown. All the stacked bed loci lie below the uniform case: a bigger region of stable operation as indicated by the vertical arrowed lines. The blue curve represents the inflection points of the first hot spot. More interesting are those of the second hot spot, shown by the red curves in Figure 1-a. This has two branches, each showing a kind of multiplicity. Only the upper parts of these branches are the relevant ones: thus, any point on the B versus $1/\psi$ plane below the blue curve (first hot spot) or red ones (second hot spot) represents exceeding the runaway boundary. In the region between the two red branches there is no inflection point before the second hot spot: the first hot spot is always limiting here.

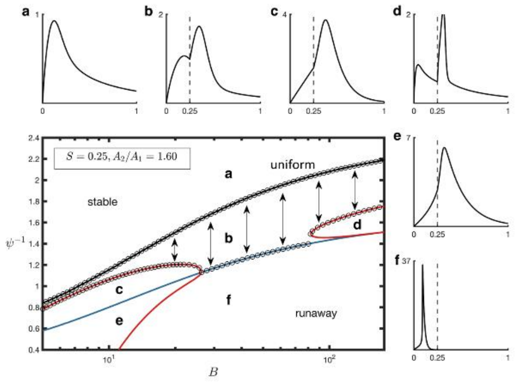

Figure 1-a. loci of the inflection points for A_2/A_1=1.6 and *S*=0.25 (reaction order n=1, dimensionless activation energy γ =1)

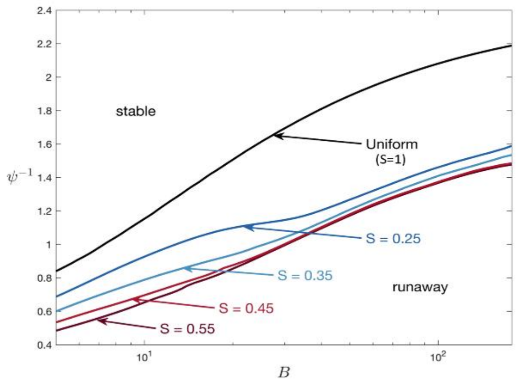

Figure 1-b. loci of the intersections, i.e. 2 inflection points coinciding (or the single inflection point).

The newly found intersection points between the loci of the inflection points of the first and second hot spot proved to be very insightful: where in Figure 1-a a red curve crosses the blue curve, the first and second hot spots are equally limiting! We subsequently hypothesized that this is the key to finding the "optimal" way of catalyst stacking with two activities for a given value of the step location *S*. In Figure 1-b, we connected the loci of the *intersections* of the inflection points, i.e. both hot spots being equally limiting for a fixed value of *S*. These intersection loci are obtained by varying the activity ratio A_2/A_1. For high *B* there can be no intersection; Figure 1-b then shows the single inflection point. For each value of *S* this gives the runaway boundary according to the definition of both hot spots being equally limiting. Figure 1-b also shows that with increasing *S* the vertical distance to the uniform activity case increases, with the maximum vertical shift occurring around *S*=0.55, slightly beyond half of the reactor length.

We further tested the hypothesis that the largest vertical distance in a plot like Figure 1-b also represents the optimal way of stacking. For this we explored two alternative objective functions: one relating to maximizing conversion and one to maximizing STY. This also revealed a dependency on how the potential benefit is achieved in practice: by increasing the throughput, the coolant temperature or both.

4. Conclusions

A methodology has been developed to generalize the classic Barkelew type diagrams for cases of catalyst activity stacking. As guidance for optimal stacking configuration one can make use of the intersection of the loci of the inflection point of the first hot spot and that of the second hot spot, reflecting the situation where both hot spots are equally limiting. This generic guidance and the modified diagrams may serve as a quick screening tool to assess for any application whether stacking of catalyst activity has potential to significantly increase the reactor productivity.

References

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Keywords

Multi-tubular reactors; Optimal stacking; Runaway diagram; Activity profiling.