

Generalized Runaway Diagrams for Catalytic Reactors with Stacked Catalyst Activities

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Abstract

Stacking of two or more catalyst beds with different activities is an option to increase the maximum productivity in wall-cooled catalytic reactors that are limited by thermal stability. The theory for thermal stability in such reactors for a uniform catalyst activity is well established. However, little work has been done towards a generic criterion for thermal runaway in the case of stacked catalyst beds, for which typically there will be two hot spots rather than just one in the case of a single exothermic n^{th} -order reaction. In the present work, we present a first attempt to extend a classical methodology of constructing runaway boundaries (Barkelew type plots) for the case of two activities, with as additional degrees of freedom the ratio of the two catalyst activities and the dimensionless stacking location. We report novel phase diagrams showing the effect of stacking on the runaway boundaries, i.e. the shift of this boundary as a function of the activity ratio and stacking location. From this, a guideline for optimizing the activity profile emerged: under the constraint of two activities and constant total activity, the maximum lowering of the runaway boundary is obtained when both catalytic zones are equally limiting. Moreover, a dimensionless step location of around 0.55 appears to be optimal, virtually independent of the other dimensionless numbers. The novel “modified Barkelew” plots can be used to quickly assess whether, for a specific application, there may be a benefit in the stacking of catalysts with different activities, to boost the reactor productivity.

Nomenclature

ΔH_R	Heat of reaction, J K ⁻¹ mol ⁻¹
A	Catalyst activity distribution, dimensionless
B	$\beta\gamma$, heat generation power, dimensionless
C_A	Molar concentration of reactant A in the fluid phase, mol m ⁻³
c_p	Average mean molar heat capacity, J K ⁻¹ kg ⁻¹
Da	$k(T_c)C_{A0}^{n-1}L/u_0$, Damköhler number, dimensionless
d_t	Reactor tube diameter, m
E_a	Activation energy, J mol ⁻¹
k	Pre-exponential factor, (mol m ⁻³) ¹⁻ⁿ s ⁻¹ kg _{cat} ⁻¹
L	Total length of the catalyst bed, m
n	Reaction order, dimensionless
R	Universal gas constant, J K ⁻¹ mol ⁻¹
S	Stacked bed activity step location, dimensionless
St	$4UL/d_t u_0 \rho c_p$, Stanton number, dimensionless
STY	Space-time yield based on catalyst bed volume, mol m ⁻³ s ⁻¹
T	Temperature, K
T_c	Coolant temperature, K
U	Overall heat transfer coefficient, W m ⁻² K ⁻¹
u	Superficial velocity, m ³ m ⁻² s ⁻¹
X_A	Conversion of reactant A , dimensionless
z	Axial coordinate, m
Z	z/L , dimensionless axial coordinate, dimensionless

Subscripts

0	Reactor inlet conditions
1	First zone of the full catalyst bed
2	Second zone of the full catalyst bed

Superscripts

*	Hot spot conditions
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Greek Symbols

β	$(-\Delta H_R)C_{A0}/\rho c_p T_c$, adiabatic temperature rise, dimensionless
γ	E/RT_c , Arrhenius number, dimensionless
θ	$(T - T_c)E/RT_c^2$, temperature, dimensionless
ρ	Density of the fluid, kg m^{-3}
ρ_b	Catalyst bed density, $\text{kg}_{\text{cat}} \text{m}^{-3}_{\text{bed}}$
ψ	$B Da/St$, Semenov number, dimensionless

1 Introduction

Wall-cooled multitubular fixed-bed catalytic reactors (MTRs) are one of the workhorses within the petrochemical industry, e.g., for ethylene oxide production and Fischer-Tropsch synthesis [1,2]. Often, the optimal design of such a reactor for strongly exothermic reactions is governed by effectively managing the heat. Specifically, to achieve high conversions, commercial reactors typically operate near the edge of thermal stability [3], e.g., at 5 or 10 K from “runaway”. The precarious balance between heat generation and heat removal can be characterized by so-called “parametric sensitivity”, in which relatively minor fluctuations in process parameters can result in large variations in, for example, hot spot temperature and conversion, i.e. resulting in a thermal runaway [4]. The theory for thermal stability in such reactors for a uniform activity is well established see for example the groundbreaking early work by Semenov [5,6], Barkelew [7], Dente and Collina [8], the more advanced work by Van Welsenaere and Froment [9], Morbidelli and Varma [10], Westerink and Westerterp [11] and their contemporaries [12-15].

To enhance the thermal stability of MTRs, or rather to increase the maximum conversion or reactor productivity, numerous strategies have been explored in practice. One particularly promising approach is applying a stacked bed of two or more catalysts with different activities, see e.g. Pirkle Jr and Wachs [16], Kosaka et al. [17], Sadhukhan and Petersen [18] and others [19-24], as well as the patent literature, for example, Schoonebeek et al. [25] and Bos et al. [26]. In the case of parametric sensitivity, the critical place in the reactor where the runaway takes off is around the hot spot: when operating at a margin to runaway of e.g. 5 or 10 K it can be observed that the region downstream of the hot spot is not in a parametrically sensitive state. Thus, having a lower catalyst activity around the hot spot and a higher activity downstream of the hot spot may increase the overall thermal stability, and hence increase the conversion and productivity (at the same margin to runaway).

Activity profiling involves strategically distributing catalysts with different (effective) volumetric bed activities along the axial direction of the reactor. This can be achieved in practice not only by different catalyst formulations but also by physically diluting the bed with inert particles or by using different particle sizes. Early research [16-18] has successfully demonstrated that by diluting the catalyst bed in the hot spot region, it is possible to mitigate the

formation of extreme hot spots and reduce parametric sensitivity. In terms of reactor performance metrics, Sofekun et al. [27] have devised a generalized equation for the prediction of the effects of catalyst dilution on conversion for positive-order reactions. Experiments at a full-scale single-tube pilot plant for oxidative dehydrogenation of ethane conducted by Shell [26] showed that catalyst activity stacking increased the maximum achievable space-time yield (STY). Also, Hwang and Smith [28] have observed several advantages of catalyst activity stacking: lowering of catalyst expenses, increased STY, and reduced hot spot temperatures minimizing undesired side reactions.

More recent work has focused on further refining these findings and optimizing the catalyst activity profile for specific applications. For instance, in their detailed modelling study, using a pragmatic maximum temperature constraint, Kern and Jess [24] showed that for the commercially very relevant Fischer-Tropsch reactors, employing two zones of equal length, a Cobalt catalyst loading ratio of 23%/40% was optimal; this yielded an improvement from 38% to 51% conversion of CO per pass. Melis et al. [29] explored optimizing catalyst distribution for reactors in which both homogeneous and heterogeneous reactions occur, while Nie et al. [3] went a step further by examining the benefits of utilizing multiple catalyst zones in ortho-xylene oxidation reactors. Their numerical optimizations indicate that using three catalyst beds can significantly reduce the deviations from isothermal operation, a finding further supported by Till et al. [30] in their multi-zone optimization studies for a hydrochloric acid oxidation process. Robust on-line optimization control schemes have also been developed for packed bed reactors with nonuniform catalyst activity profiles [31,32].

Despite these studies of catalyst stacking in MTRs, we could not find publications on a generalized criterion for thermal runaway for stacked beds of catalysts with two or more activities, taking into account the additional degrees of freedom this stacking introduces. Most existing literature comprises in fact case studies and addresses thermal runaway by imposing process-specific constraints on the hot spot temperature. Applications of stacking of two, three, five or even ten activities reported in literature comprised Fischer-Tropsch synthesis [2, 24, 25], ortho-xylene oxidation [3,20], oxidation of methanol [23,33], hydrogenation of nitro-benzene and epoxidation of ethylene [28], oxidation of HCl [30] and for the energy transition more and

more relevant methanation of CO₂ [17]. While this case study type of approach proves adequate on a case-by-case basis, it does not provide a more comprehensive understanding of thermal runaway in the case of catalyst activity stacking.

In other words, what is still lacking is the stacked-bed equivalent of the classic “Barkelew-type plot” as developed for uniform catalyst activity. Another motivation for this work was based on observations within Shell, where stacking of catalysts in MTRs was explored both theoretically and experimentally for a variety of applications. The resulting increase in conversion or STY was relatively modest, typically achieving a maximum productivity gain of 10-20% (although this might still be economically attractive enough to implement in practice). This consistent finding, over a range of different case studies, raised the question of whether this applies generally, or was merely due to the specifics of the application at hand. A Barkelew-type plot might not only shed light on this but also provide a screening tool to assess whether a more detailed study is warranted for each specific application.

2 Methodology

2.1 Definition of thermal runaway

Analogous to other phenomena in chemical processes, thermal runaway arises from the interactions of dimensionless groups that dictate system stability. Recognizing this, we sought to develop a methodology that leverages these dimensionless groups to comprehensively describe the onset of thermal runaway, building on the approaches used for MTRs with catalyst beds of uniform activity as referenced in the introduction. The various alternative runaway criteria can be broadly categorized into geometry-based, sensitivity-based, and explicit criteria, see Kummer and Varga [34]. Geometry-based criteria are derived from observing geometric features of variable profiles, for example, defining the onset of thermal runaway as the occurrence of an inflection point before the temperature maximum (hot spot) on the temperature-reactor axial coordinate plane. By contrast, sensitivity-based criteria quantify the parametric sensitivity of the system using normalized sensitivity variables. Other approaches derive explicit algebraic criteria describing the limit of thermal runaway. The different results from a selected number of such

runaway criteria are plotted and compared in Fig. 1. Usually, the region outside “runaway” is denoted as a “safe operating regime”. We will use the word “stable” instead, to avoid the suggestion that the reactor may become “unsafe”: industrial plants are typically designed to safely cope with these runaways (or any other possible type of runaway). The dimensionless groups involved are explained in more detail further on, but in essence, the x -axis reflects the dimensionless heat production potential, and the y -axis the dimensionless heat removal potential over the heat production potential. Plots like Fig. 1 show the runaway boundary as a function of carefully chosen dimensionless parameters, where in this case B , defined by Eqn. (4), combines the dimensionless heat of the reaction with the sensitivity of its rate to temperature, and ψ is the Semenov number, defined by Eqn. (5). Such a plot will be henceforth referred to as “a Barkelew plot”. Operating closer to the runaway boundary typically yields higher conversions and higher productivity. Thus, for the case of non-uniform activity, we hope to move the runaway boundary in a Barkelew plot significantly downwards.

The various alternative mathematical definitions of a runaway boundary in the uniform activity case can also be directly applied to constructing the corresponding boundary in the stacked activity case. For example, Quina and Quinta Ferreira [33] analyzed the region of thermal stability in an MTR for partial oxidation of methanol with catalyst activity stacking via catalyst dilution, applying the sensitivity-based criterion developed by Morbidelli and Varma [10].

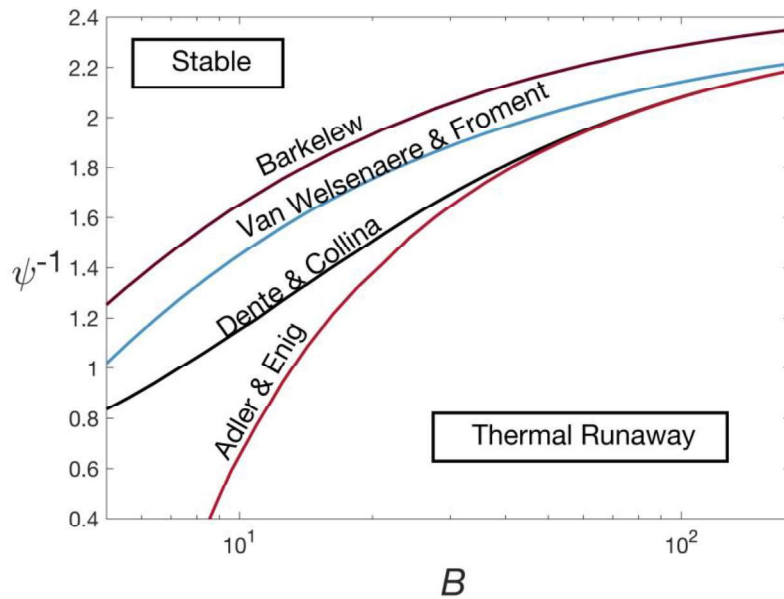


Fig. 1 Runaway boundaries for uniform activity profile and $n = 1$, $Da = 1$, $\gamma = 10$, where above the boundaries is a safe operation and below the boundaries is a parametrically sensitive operation, or thermal runaway. Selected runaway criteria examples by Barkelew [4,7], Dente and Collina [8], Van Welsenaere and Froment [9], and Adler and Enig [12].

Some studies also take selectivity effects into account, see e.g. Westerink and Westerterp [11]. In this work, we adopted a geometry-based criterion, namely the occurrence of an inflection point before a hot spot, i.e. the one originally proposed by Dente and Collina [8]. A key challenge here is that for the catalyst activity stacking case there will in general be multiple hot-spots.

Therefore, in this work, the stacking configuration is limited to two activities, hence a maximum of two hot spots, with the additional constraint of maintaining the total activity in the reactor the same as the uniform case (or only permitting a lower activity in the upstream section of the bed). Even with these simplifications, two new degrees of freedom are introduced: the ratio of the activities in the two sections, and the location of the step change in activity.

2.2 Model equations

We chose a model suitable for this study, which does not deviate fundamentally from those classically applied to the uniform activity case. Therefore, in this work, we use the steady-state one-dimensional pseudo-homogeneous model with an n^{th} -order irreversible reaction, without axial dispersion. In fact, Westerink et al. [35] showed that with an appropriate lumping parameter, this one-dimensional model is almost equivalent to the two-dimensional model, except for high Biot numbers. Alternatively, a 1-D *heterogeneous* model, which takes particle scale heat transfer limitations into account, may yield significantly different runaway boundaries, for example, Balakotaiah and Luss [36], even though generally these limitations are small or even negligible at the commercial scale. At high Reynolds number common in commercial practice, the reactor is typically operated at a significant “margin to runaway” where both the particle scale limitation, as well as the 2-D effect, are usually quite small. When pushed to the runaway boundary, these effects become much more pronounced, especially in the hot spot. This explains that indeed the runaway boundary for a 2-D model or a heterogeneous model can be significantly different quantitatively compared to the classic 1-D pseudo-homogeneous model. However, in this paper, we chose that latter model to enable direct comparison with the classic

works and because the purpose of our paper is *not* to accurately predict the runaway boundary itself, but primarily to map the potential of stacking of catalyst activity.

A uniform coolant temperature T_c is assumed and the reactor inlet temperature T_0 is set equal to that of the coolant. These are common assumptions employed by most other authors analyzing thermal runaway; in fact, in authors' experience it hardly makes a difference for the reactor performance if T_0 is somewhat lower as often done in industrial practice for heat integration purposes, i.e. the very first part of the bed pre-heats the feed to T_c .

To introduce stacking of catalyst activity, an activity parameter A is defined, being unity throughout the bed for the case of uniform activity and varied with reactor length for the stacked bed. Appendix 1 gives the original dimensional form of the model; the model equations in non-dimensional form are:

$$\frac{dX_A}{dZ} = A Da \exp\left(\frac{\theta}{\theta/\gamma + 1}\right) (1 - X_A)^n \quad (1)$$

$$\frac{d\theta}{dZ} = A B Da \exp\left(\frac{\theta}{\theta/\gamma + 1}\right) (1 - X_A)^n - St \theta \quad (2)$$

$$\text{with boundary conditions } X_A(0) = 0; \theta(0) = 0 \quad (3)$$

where X_A , θ and Z are the conversion, the dimensionless temperature and the axial position, respectively. The dimensionless groups characterizing the system are the adiabatic temperature rise, activation energy (combined as B , the heat generation power), Damköhler and Stanton number:

$$\beta = \frac{(-\Delta H_R)C_{A0}}{\rho c_p T_c}; \gamma = \frac{E_a}{RT_c}; B = \beta\gamma; Da = \frac{\rho_b k(T_c)C_{A0}^{n-1}L}{u_0}; St = \frac{4UL}{\rho c_p d_t u_0}.$$

As introduced previously, Fig. 1 shows for various definitions of runaway, the boundary of stability for uniform catalyst activity, for a fixed n , γ , and Da . The x -axis, B , is the product of the

dimensionless adiabatic temperature rise and the dimensionless activation energy. For a typical reaction, which would call for the selection of a wall-cooled tubular reactor, the coolant temperature is often in the range of 300 – 800 K, with adiabatic temperature rise range from 100 to 1000 K, and activation energy between 50 and 250 kJ mol⁻¹. In combination, these typical values result in an extreme range of B from 1 to 500; however, for nearly all large scale petrochemical processes, B tends to be between 10 and 50. The y-axis of Fig. 1 is the reciprocal of the Semenov number, ψ^{-1} , defined as:

$$\psi^{-1} = \frac{St}{B Da} \quad (4)$$

which captures the relative magnitudes of the heat-removal and the heat-release potential of the system. For an MTR with uniform activity, given parameters B (characterizing the heat released in the reaction) and St (characterizing the cooling intensity of the reactor), a runaway boundary in Fig. 1 directly provides the maximum Damköhler number, Da , for stable operation. Hence, a downward shift of the runaway boundary enables a higher Da , i.e. higher conversion or STY, by allowing T_c and therefore the rate constant k to be increased.

For catalyst activity stacking, $A(Z)$ is the activity profile, which increases or decreases the reaction rate of the catalyst at position Z in the bed, compared to the standard catalyst used in the bed of uniform activity. For uniform activity, A is unity along the entire length of the bed, whilst with stacking of two zones of catalyst activity, A is a stepwise function with a step at dimensionless bed length S :

$$A = \begin{cases} A_1, & \text{for } 0 < Z < S \\ A_2, & \text{for } S < Z < 1 \end{cases} \quad (5)$$

Adapting Dente and Collina's [8] definition of thermal runaway for the uniform activity case, runaway is (numerically) identified by the emergence of an inflection point before the hot spot temperature θ_1^* of the first zone or θ_2^* of the second zone:

$$\frac{d^2\theta}{dZ^2} = 0, \quad Z \in [0, Z|_{\theta_1^*}] \cup [S, Z|_{\theta_2^*}] \quad (6)$$

This definition anticipates that there can be up to two hot spots, each with its own inflection point before the hot spot. To optimize performance metrics such as conversion, the optimization algorithm searched for an activity profile and an operating point as close as possible to this runaway boundary without crossing it. However, this approach often resulted in a moderate activity level A_1 to significantly deplete reactants in the first zone, and an unrealistically high value of A_2 to ensure complete consumption of remaining reactants in the second zone. To ensure a fair evaluation of the potential benefit of a stacked bed, we impose an additional equality constraint:

$$A_1 S + A_2 (1 - S) = 1 \quad (7)$$

This constraint requires that the total amount of catalyst (that is, active material) remains the same before and after the activity profiling, thereby maintaining balance and realism in the modeling process as e.g. Kern and Jess [24] also pointed out. Furthermore, Eqn. (7) ensures that the value of Da for a uniform bed retains some relevance to the stacked bed (in this case Da being based on the average activity of 1). Whilst in practice this is a somewhat arbitrary constraint, it does not undermine our findings. We will demonstrate later that similar behavior is obtained in case of dilution of the catalyst in the first zone, i.e. lowering A_1 only and keeping A_2 at 1.

Therefore, two variables are required to characterize a catalyst activity profile. The relative activity ratio A_2/A_1 and the step location S are chosen to be the decision variables since, as will be addressed, S is a crucial variable dominating the thermal runaway behavior, and A_2/A_1 provides a convenient insight to the relative catalyst activities in both parts of the bed.

Appendix A provides details on the numerical procedure to produce the Barkelew plots presented in this paper.

2.3 Effect of operator's handles on the location in a Barkelew plot

Anticipating that stacking of catalyst activity yields a shift down of the runaway boundary in a Barkelew plot, there are several ways that the expansion of the stable operating region could be exploited in practice. For an existing plant, stacking could allow for higher per-pass conversion or higher throughput (or both). Variables such as the reactor coolant and inlet temperature $T_c = T_0$ and the superficial velocity u_0 , i.e. throughput for an existing plant, are the most manageable to manipulate. Other parameters are predetermined either by the reaction scheme e.g. activation energy E_a , rate constant $k(T_c)$, heat of reaction ΔH_R , or the physical dimensions of the reactor (length L and tube diameter d_t). Changing the superficial velocity affects equally the parameters Da and St , thus the effect of u_0 cancels out in the Semenov number, as can be seen from Eqn. (4). However, in practice the heat transfer coefficient U depends on the particle scale Reynolds number thus on u_0 . Hence, the parameters St and Semenov number depend indirectly on the superficial velocity u_0 in a somewhat complex way. Therefore, we first focus on the effect of exploiting the potential benefit of stacking, by increasing the coolant temperature compared to the uniform activity case, thereby increasing the reaction rate and so conversion.

Clearly, the key dimensionless parameters γ , Da and B are all affected by changes in T_c . Fortunately, since this is usually well above 300 K, more typically 500 – 800 K, the impact of increasing T_c by e.g. 5 – 20 K on those parameters is relatively small. For example, starting with $B = 50$, $Da = 1$, $\gamma = 10$ and $\psi^{-1} = 0.9$ (i.e. just above the runaway boundary of Dente and Collina in Fig. 1 for a uniform bed, with $n = 1$), increasing T_c from 500 to 520 K results in a decrease in ψ^{-1} to 0.66, and B to 46.5, i.e. a relatively small shift to the left compared to the shift down along the logarithmic x-axis of Fig. 1. Therefore, in the Barkelew plot, increasing T_c is approximately equivalent to a vertical movement downwards, i.e. a reduction in ψ^{-1} at virtually constant B . In this first approximation, the effect of T_c on the Semenov number is equivalent to the effect of St ; this equivalence greatly simplifies the interpretation of the Barkelew plots for the stacked beds. There are two caveats to this: firstly, in the example above Da increases from 1 to 1.5. This does not affect the Barkelew plot for a uniform bed, because the effect of Da on the runaway boundary is fully built into the Semenov number. However, since the stacked bed is not fully characterized by a single Da , the runaway boundary does depend on Da to some extent. Secondly, γ decreases from 10 to 9.6, which in fact shifts the runaway

boundary on a Barkelew plot, even for a uniform bed (although this dependence is not always explicitly reported in the literature). Consequently, we investigated the sensitivity of our conclusions with respect to the parameter values Da and γ as well as the reaction order n .

3 Results and discussion

3.1 Runaway boundary for catalyst activity stacking

Applying the runaway criterion of an inflection point before a hot spot, over a wide range of B (and initially with $n = 1$, $Da = 1$ and $\gamma = 10$), it was found that the runaway boundaries on Barkelew plots for stacked catalyst activities can be classified in three distinct types. Each one has the appearance of a phase diagram for substances, but with each region representing runaway behavior of a subtly different nature, therefore these plots are referred to henceforth as “phase diagrams”.

Fig. 2 exemplifies a Type I phase diagram, the simplest of all three. This behavior tends to emerge when the activity in the first zone is slightly lower than unity, and the two zones are of roughly equal size. In Fig. 2 this Type I behavior is shown for an activity ratio $A_2/A_1 = 1.6$ and a dimensionless step location of $S = 0.4$, corresponding to $A_1 = 0.74$ and $A_2 = 1.18$. It can be seen that for all values of B , the runaway boundary has shifted down compared to the uniform activity case, i.e. it shows that there is potential for an increase in coolant temperature and thus conversion (the benefit with respect to conversion is quantified in Section 3.2). Fig. 2 also depicts the axial temperature profiles corresponding to the three regions **a-c** in the phase diagram. In region **a** both the stacked bed and uniform bed are stable, and a single hot spot emerges. In region **b** the uniform bed is in runaway, but the stacked bed is still stable. In this region, there are two hot spots. Finally, in region **c** the stacked bed is also in runaway for $A_2/A_1 = 1.6$ and $S = 0.4$.

The key feature of this Type I behavior is that runaway always occurs in the first “ A_1 zone”, i.e. there never is an inflection point before the hot spot in the “ A_2 zone”.

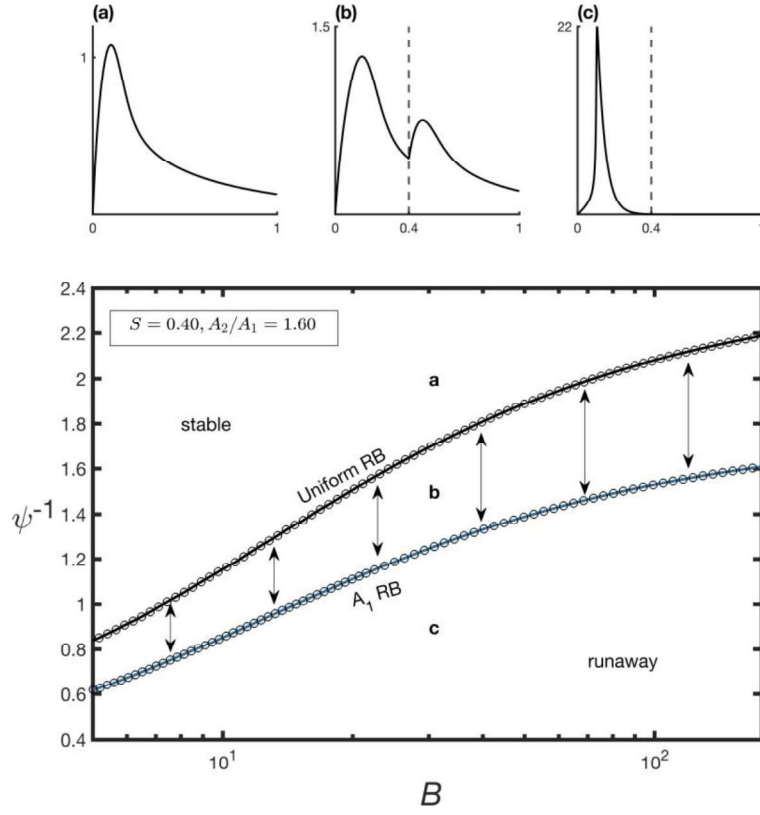


Fig. 2. Example of a Type I phase diagram

Runaway boundary plot at $n = 1$, $Da = 1$, $\gamma = 10$ for catalyst activity profile $A_2/A_1 = 1.60$ and $S = 0.40$, with associated temperature profile examples. Lines highlighted with circles denote stable operating points. RB = Runaway Boundary. Typical axial profile for each region a-c shown in (a) stable operation under uniform activity profile with $B = 30$ and $St = 60$; (b) stable operation under stacked activity profile with $B = 30$ and $St = 42$; (c) thermal runaway in the first zone under stacked activity profile with $B = 30$ and $St = 24$.

The Type II phase diagram is more intricate, exemplified by Fig. 3. Here there can be an inflection point before the hot spot in the first zone, in the second zone, or in both. Again, just as an example, Type II behavior emerges when using the same activity ratio as used for Fig. 2, but moving the step location closer to the inlet, in this case $S = 0.25$ instead of 0.4. As dictated by Eqn. (8), this results in a decrease in A_1 to 0.69 compared to 0.74 in the Type I scenario. Fig. 3 presents the resulting Type II behavior over a large range of B . The phase diagram in Fig. 3 shows six distinct regions, comprised of two envelopes and a connecting single runaway boundary in between. For the stacked activity bed, there are two runaway boundaries ("A₁ RB" and "A₂ RB"): the trajectories of the inflection point of the first and second zone respectively. The lines highlighted with circles denote the boundary of stable operating points of the reactor,

i.e. below this circled boundary the reactor is in runaway either due to an inflection point in the first or in the second zone. This is clarified in Fig. 3 by the axial temperature profiles corresponding to each region **a-f** in the phase diagram. In general, with less reactant being consumed in the first zone than before, the feed to the second zone has a higher concentration of reactant. This increase in reactant concentration, combined with the more active catalyst in the A_2 zone, required to satisfy Eqn. (8), is sufficient to potentially trigger a thermal runaway in the A_2 zone.

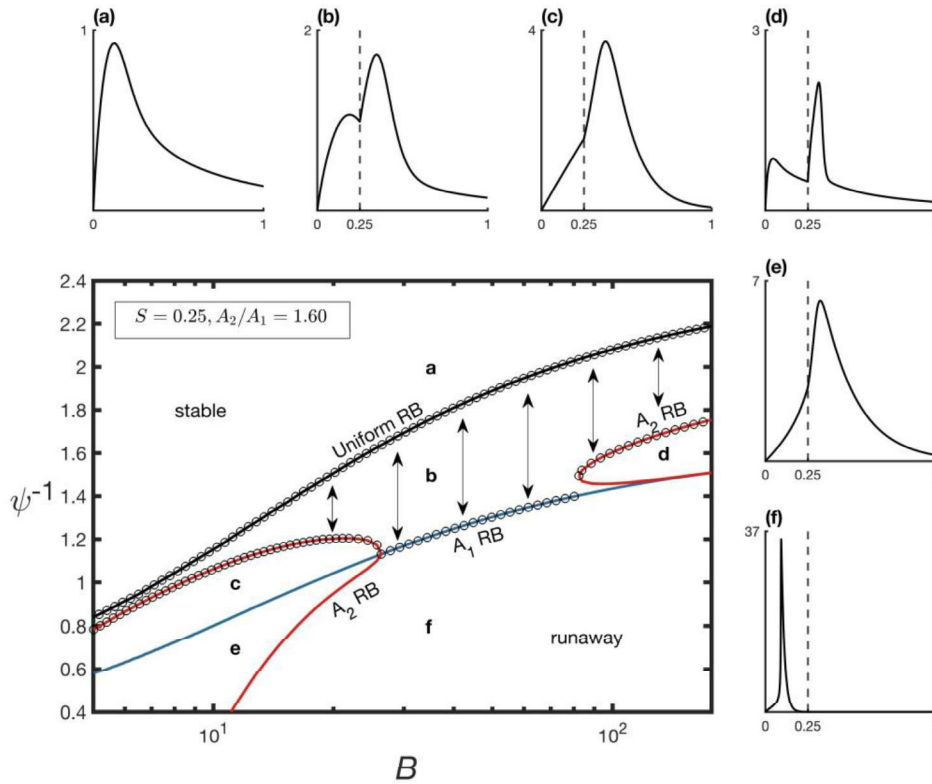


Fig. 3. Example of a Type II phase diagram

Runaway boundary plot at $n = 1$, $Da = 1$, $\gamma = 10$ for catalyst activity profile $A_2/A_1 = 1.60$ and $S = 0.25$, with associated temperature profile examples. Lines highlighted with circles denote the boundary of stable reactor operating points. RB = Runaway Boundary. Typical axial profiles for each region a-f shown in (a) stable operation under uniform activity profile with $B = 20$ and $St = 40$; (b) stable operation under stacked activity profile with $B = 20$ and $St = 26$; (c) thermal runaway in the second zone under stacked activity profile with $B = 10$ and $St = 8$; (d) thermal runaway in the second zone under stacked activity profile with $B = 120$ and $St = 200$; (e) thermal runaways in both zones under stacked activity profile with $B = 10$ and $St = 5$; (f) thermal runaway in the first zone under stacked activity profile with $B = 50$ and $St = 55$.

In region **b** and for the lower values of B , the stacked bed is still stable, but moving down to region **c**, the temperature profile in the first zone approximates what is known as pseudo-adiabatic operation (PAO) [37]. Here the temperature rises monotonically, culminating in a high

final temperature upon entering the A_2 zone. Therefore, this second zone is characterized by high inlet temperatures and concentrated reactants, which combined with the increased catalyst activity, facilitates the formation of a runaway envelope, regions **c** and **e**. Interestingly, as shown in Fig. 3(c), moving down from region **b** to **c**, the “limiting” hot spot is no longer in the first A_1 zone, but in the second A_2 zone. In region **e**, although not immediately evident from the temperature profile in Fig. 3(e), both zones are in fact in runaway.

In contrast, at the moderate values of B in Fig. 3, we only have stable regions **a** and **b**, and an unstable region **f**, i.e. there is no runaway in the A_2 zone. In this case, not unlike Type I stacking, the heat generated by the reaction causes the first zone to enter a classic hot spot operation (HSO) [37], and the first hot spot is again the limiting one. Henceforth, we will refer to the upper boundary line of this envelope connecting regions **b** and **c** as the A_2 boundary, and **b** and **f** as the A_1 boundary. At high values of B , the enhanced heat of reaction amplified by high catalyst activity in the A_2 zone can induce thermal runaway in that zone before the occurrence of an inflection point in the A_1 zone, leading to the formation of another envelope indicated by region **d** in Fig. 3. We will refer to the upper boundary between **b** and **d** where the second hot spot is limiting as the A_2 boundary. Moving down through region **d** into **f**, the first hot spot is limiting once again.

One of the first important insights obtained from Fig. 3 involves both the mathematical and physical meaning of the intersection points. For low values of B , at the intersection where regions **b**, **c**, **e** and **f** come together, there is an inflection point simultaneously in the first and second zones, i.e. both hot spots are equally limiting. In the next section, we will exploit this feature of coinciding inflection points of the first and second hot spots. For high values of B , there is a small, approximately triangular region where **b**, **d** and **f** converge. However, operating within the triangular region is not advisable, as any minor fluctuations in process parameters either up or down will trigger thermal runaway, and hence the classic strategy to operate at e.g. 5 or 10 K “margin to runaway” would not work in industrial practice.

Finally, the Type III stacking behavior shown in Fig. 4 was discovered by further reducing A_2/A_1 to 1.60. With decreasing S , the envelopes **c/e** and **d** in Fig. 3 progressively approach each

other, eventually merging into a single boundary. For lower values of S the A_2 zone is in runaway. This boundary, separating regions **b** and **c**, is similar in nature to the A_1 boundary in the Type I phase diagram; however, it can be seen in Fig. 3 that these boundaries for the uniform bed and the stacked bed cross over, in this case at $B \approx 15$. Clearly, the boundary for the stacked bed almost coincides with the one for uniform activity, thus the advantage of stacking is much lower here. Moreover, for very low B the stacked bed is even worse than the uniform bed. Within regions **c**, **d** and **e** in Fig. 3, either the A_2 zone or both zones of the stacked bed are in thermal runaway, i.e. for Type III behavior there is no stable operating point where the A_1 and A_2 zones are equally limiting.

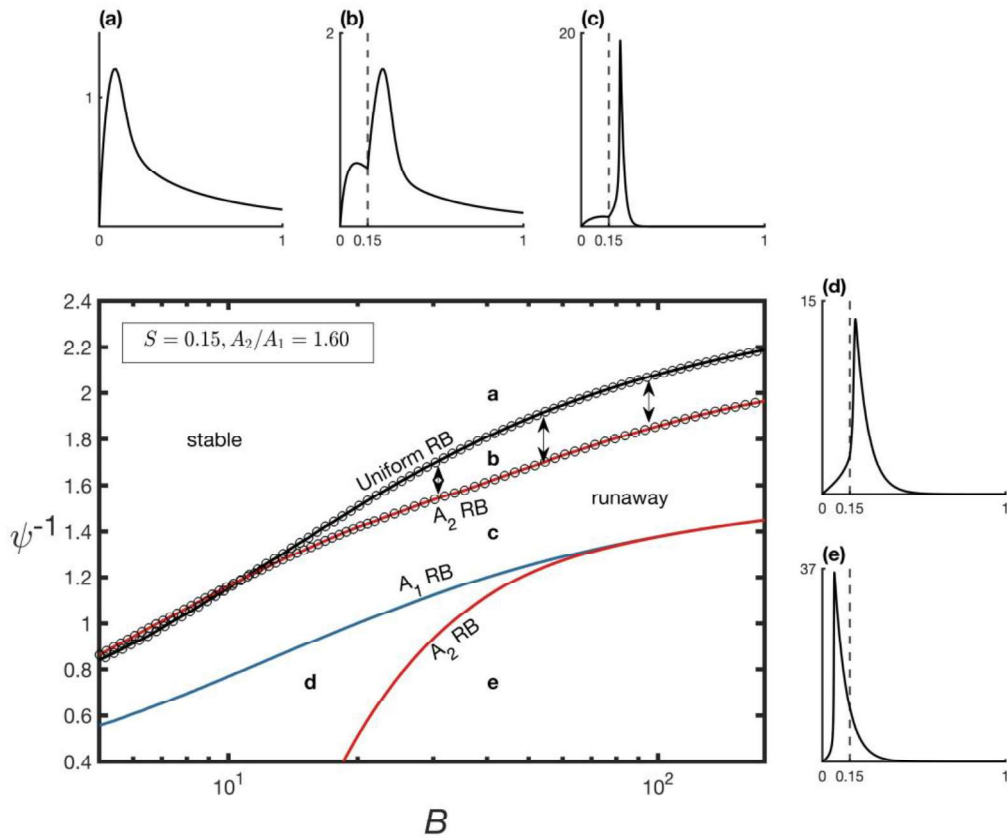


Fig. 4. Example of a Type III phase diagram

Runaway boundary plot at $n = 1$, $Da = 1$, $\gamma = 10$ for catalyst activity profile $A_2/A_1 = 1.60$ and $S = 0.15$, with associated temperature profile examples. Lines highlighted with circles denote stable operation. RB = Runaway Boundary. Typical axial profiles for each region a-e are shown in (a) stable operation under uniform activity profile with $B = 40$ and $St = 80$; (b) stable operation under stacked activity profile with $B = 40$ and $St = 68$; (c) thermal runaway in the second zone under stacked activity profile with $B = 40$ and $St = 56$; (d) thermal runaway in both zones under stacked activity profile with $B = 20$ and $St = 15$; (e) thermal runaway in the first zone under stacked activity profile with $B = 40$ and $St = 15$.

3.2 Conversion improvement in a stacked bed

The degree of conversion improvement that can be realized in a stacked bed by e.g. increasing T_c hinges on the extent to which the local heat production can be lowered in the A_1 zone without triggering thermal runaway in the higher activity A_2 zone. This relationship is clearly illustrated in the previous phase diagrams of Figs. 2 to 4: for any given value of B and many stacking configurations (defined by A_2/A_1 and S), the A_1 runaway boundary shifts to lower values of ψ^{-1} . Conversely, certain suboptimal stacking configurations can have adverse effects, because of the emergence of the A_2 runaway envelopes impose restrictions on how much ψ^{-1} can be reduced at certain values of B . This can even render the stacked bed unstable under conditions where the uniform bed would be stable, e.g. the runaway boundaries for low values of B in Fig. 4.

In the previous sections, just for illustration purposes, we explored only a few values of S with an activity ratio $A_2/A_1 = 1.60$ to introduce the three different types of “phase diagrams” we uncovered. The higher-level objective is to find the optimal activity stacking strategy, the optimal A_2/A_1 and S , dependent on B : how to choose the activity profile in order to maximize the benefit of stacking, e.g. in terms of conversion improvement. One interesting observation from the runaway boundary plots with Type II behavior is that where the runaway boundaries of zones A_1 and A_2 intersect, both beds are equally limiting at these points of intersection *viz.* both zones are at the verge of runaway. We hypothesized that such an intersection, whereby both hot spots are equally limiting, represents for that particular stacking configuration the point in the Barkelew plot with the highest benefit as a function of B . To test this hypothesis, we examined examples of stacking configurations as previously shown in Figs. 2 to 4. In this part of the study, the dimensionless groups n , γ , Da , and the activity profile parameters A_2/A_1 and S were fixed. The objective was to identify the value of B and the corresponding minimum ψ^{-1} for stable operation, that yields the largest improvement in terms of conversion. Such a conversion improvement can be defined in different ways, e.g. absolute increase in conversion percentage points, relative increase in degree of conversion X , or relative decrease in unconverted reactant $(1 - X)$. In this work, we used:

$$\% \text{ Improvement} = \frac{X_{\text{stack}} - X_{\text{uniform}}}{X_{\text{uniform}}} \times 100 \quad (8)$$

where X_{stack} and X_{uniform} are the highest conversions achievable without inducing thermal runaway for stacked and uniform activity, respectively. In other words, these are the conversions achieved on the lowest feasible points on the Barkelew plots, indicated by the circled operating points in Figs. 2 to 4.

Fig. 5 superimposes the resulting improvement in conversion, onto the Type II phase diagram of Fig. 3. Clearly, the optimal improvement emerges near the intersection point between A_2 envelope and A_1 . Additionally, there is another local maximum on the higher envelope of the A_2 boundary. We noted that the maximum improvement in conversion of 7.1% at the lower B and the local maximum of $\sim 4.6\%$ at higher B was indeed at the point where both the A_1 and A_2 zones were equally limiting, at those particular values of B .

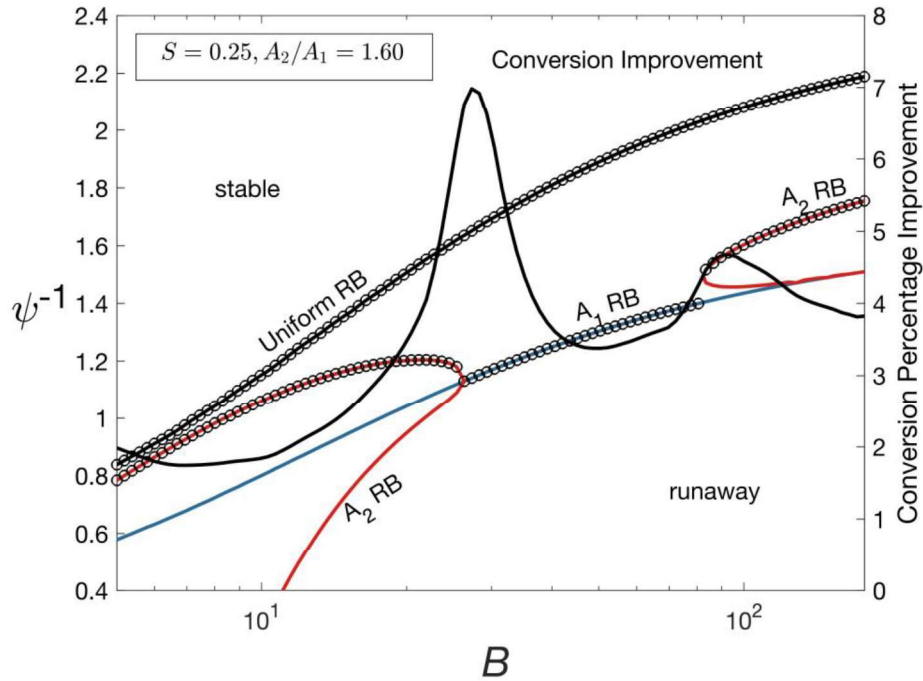


Fig. 5. Conversion improvement plots superimposed on the thermal runaway boundaries at $n = 1$, $Da = 1$, $\gamma = 10$. RB = Runaway Boundary, for $S = 0.25$ and $A_2/A_1 = 1.60$, featuring maximum improvement in conversion when runaway boundaries intersect.

In addition, for Type I phase diagrams, exemplified by the activity profile used to construct Fig. 2, the optimal conversion improvement is determined to be 5.4%; for Type III phase diagrams,

exemplified by the activity profile in Fig. 4, the optimal conversion improvement is determined to be 2%. Consequently, our hypothesis that the maximum conversion improvement corresponds to the A_1 and A_2 zones being equally limiting appears to hold. Thus, it remains only to establish how to design a stacking configuration that achieves this goal for any value of B . Since for both the Type I and Type III phase diagrams there is no such point where both hot spots are equally limiting, this in turn implies that the optimal activity profile would correspond to Type II behavior.

3.3 Activity profile strategies for maximum conversion increase

In searching for the activity profile for which the A_1 and A_2 zones are equally limiting, we first focus on how the locations of the intersection points depend on the ratios A_2/A_1 and S . For those combinations, which result in Type II behavior, the locations of these intersections (and only those) can be plotted in a Barkelew plot. Fig. 6(a) shows the loci of intersections for the base case parameters of $n = 1$, $Da = 1$ and $\gamma = 10$ at fixed values of S from 0.25 to 0.55. These loci of intersections are found by varying A_2/A_1 for each value of S , hence yielding the corresponding values of B and ψ^{-1} . At the lower values of B , the location plotted is the intersection of the A_2 with the A_1 boundary, whilst at high B the location is on the A_1 boundary, below the tip of the A_2 envelope, see Fig. 5. As A_2/A_1 increases, the two envelopes converge, approaching Type III behavior. The gap in the loci of intersections (e.g. at $B \approx 40$ for $S = 0.25$) is due to the numerical difficulty in accessing the precise value of A_2/A_1 at which the envelopes joined.

Alternatively, rather than focusing on the loci of intersections, the loci of the maximum vertical distance between the uniform and stacked bed boundary can be plotted. As before, these loci are obtained for each value of S by varying the ratio A_2/A_1 . The lines in Fig. 6(b) show this for the same range of step locations S . The curves derived from the two different approaches virtually coincide for all values of S ; thus, these two approaches for optimizing catalyst activity stacking appear virtually equivalent. The corresponding values of A_2/A_1 are given in Fig. 6(c).

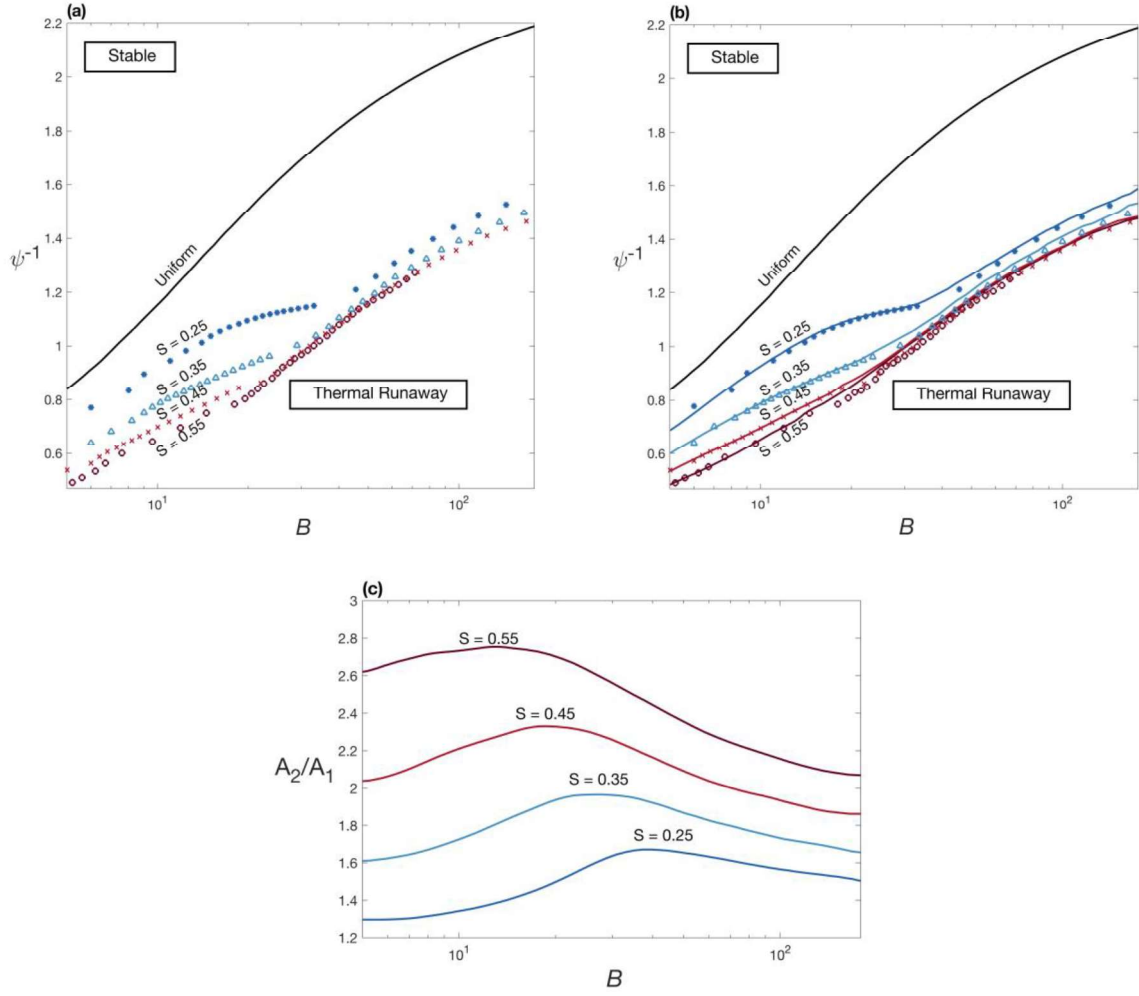


Fig. 6-a. Locus curves of the intersections for various values of S ($n = 1, Da = 1, \gamma = 10$)

Fig. 6-b. Locus curves of the maximum vertical distance approach ($n = 1, Da = 1, \gamma = 10$). Scattered points are again the loci of intersections.

Fig. 6-c. The resulting activity ratios (based on the maximum vertical distance method).

Fig. 7 shows that as S increases from 0.25 to 0.55, the vertical distance from the uniform runaway boundary also increases, especially for the lower values of B . For values of S greater than 0.55, the vertical distance decreases again. The benefit of stacking is relatively sensitive to the step location S , especially for $S < 0.4$ and $B < 30$. Thus, at least for these values of Da, γ and n , a stacking configuration with $S \approx 0.55$ offers the greatest improvement potential (or very close to it) for all values of B .

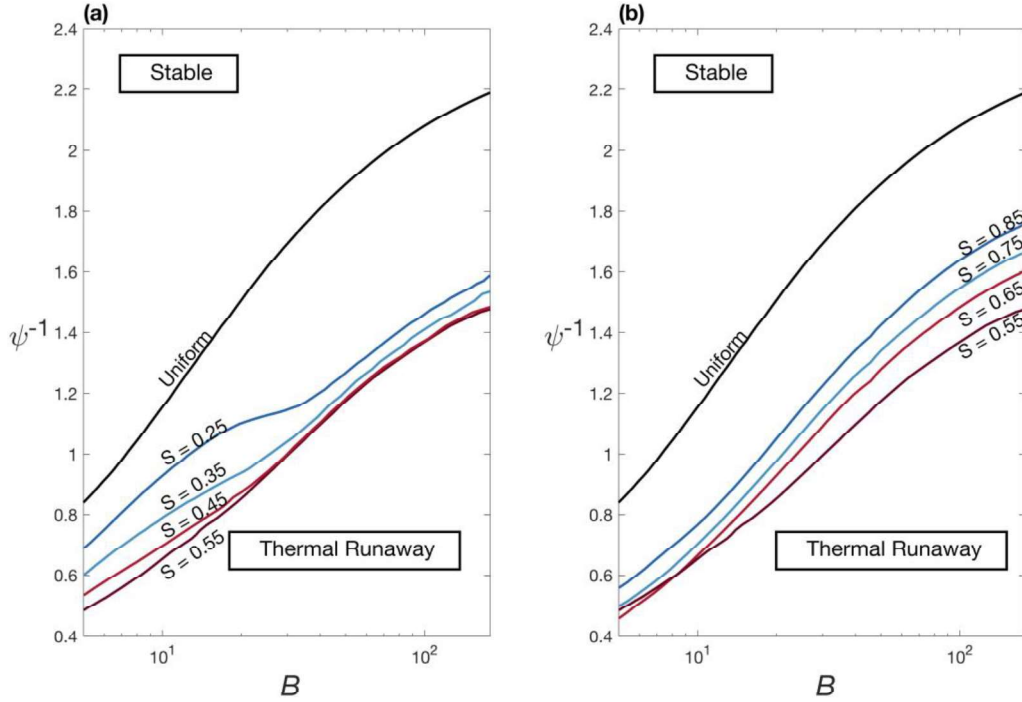


Fig. 7. Loci of maximum distance points to the uniform activity runaway boundary at various step locations S for $\gamma = 10$, $Da = 1$ and $n = 1$. a: $S = 0.25$ to 0.55 ; b: $S = 0.55$ to 0.85 .

3.4 Effect of other dimensionless groups

The fact that the runaway boundaries in a Barkelew-type plot are still dependent on e.g. γ is well known for the uniform activity case, see e.g. Van Welsenaere and Froment [9]. However, the qualitative trends remain unchanged. Studies by Varma and Morbidelli [4] also indicate that runaway boundaries of uniform catalyst activity remain relatively unchanged even as γ approaches infinity. To establish whether our stacked bed findings for the base case values of Da , γ and n were generally applicable, we extended our analysis to include different sets of these dimensionless parameters. Figures 8, 9 and 10 are Barkelew plots showing the effect of Da , γ and n respectively, on the loci of maximum vertical distance from the uniform boundary.

In Figs. 8(a) and (b) the dimensionless activation energy γ is doubled. Both the uniform activity runaway boundary and the loci of maximum vertical distance for the boundary of the stacked bed shift upwards, particularly at higher values of B , when compared to Fig. 7. In line with the

results for uniform activity, the effect is relatively small. Moreover, it can be seen that $S \approx 0.55$ remains an optimal choice (or again, very close to it) over the full range of B .

By comparing Figs. 9(a) and (b) with Fig. 7 it can be seen that reducing Da from 1 to 0.5 results in a shift upwards of the loci of maximum vertical distance for the runaway boundary. This implies that by lowering Da (e.g. via *increasing* u_0) one can move from stable operation to runaway. With stacked activity, lowering Da reduces the conversion in the first zone; consequently, there is a higher concentration of reactant entering the higher activity second zone causing an inflection point in that zone. In other words, lowering Da reduces the “shielding effect” that the conversion in the first zone has on the thermal stability of the second zone. The runaway boundary for a uniform bed is not affected by Da (because its effect is already fully incorporated in the ordinate ψ^{-1}) and hence the net effect of increased Da is that the A_2 boundaries are closer to the one for a uniform bed, reducing the potential improvement in conversion from a stacked bed. Once again, $S \approx 0.55$ remains a good choice in order to realize most or all of the benefit of stacking, even though for low values of B a slightly higher optimal value was found.

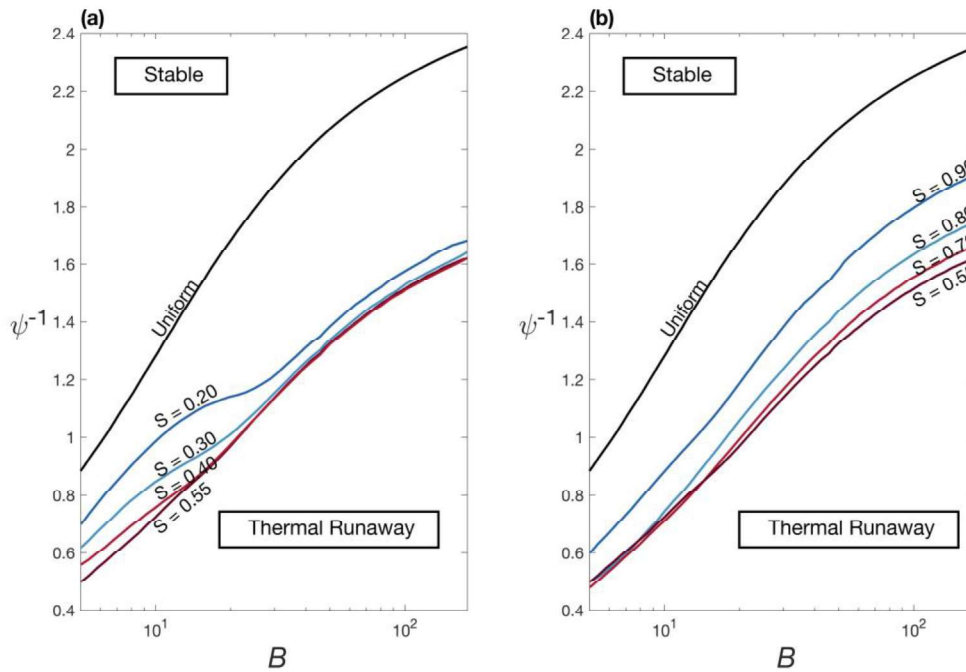


Fig. 8. Locus of maximum distance points to the uniform activity runaway boundary at various step locations S for $\gamma = 20$, $Da = 1$ and $n = 1$. **a:** $S = 0.20$ to 0.55 ; **b:** $S = 0.55$ to 0.90 .

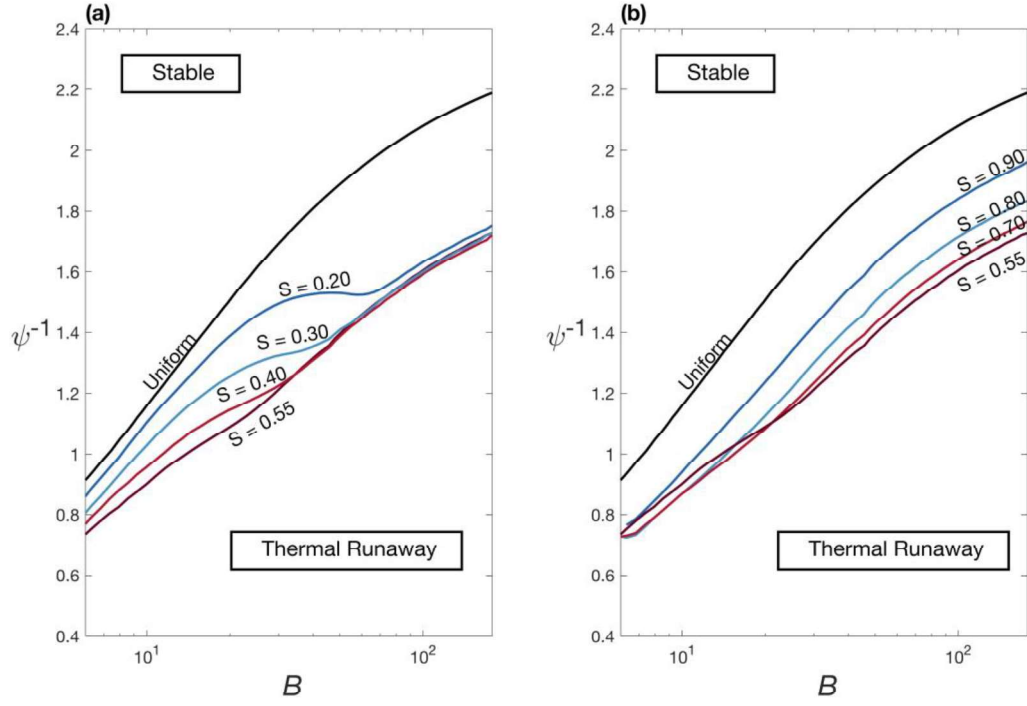


Fig. 9. Locus of maximum distance points to the uniform activity runaway boundary at various step locations S for $\gamma = 10$, $Da = 0.5$ and $n = 1$. **a:** $S = 0.20$ to 0.55 ; **b:** $S = 0.55$ to 0.90 .

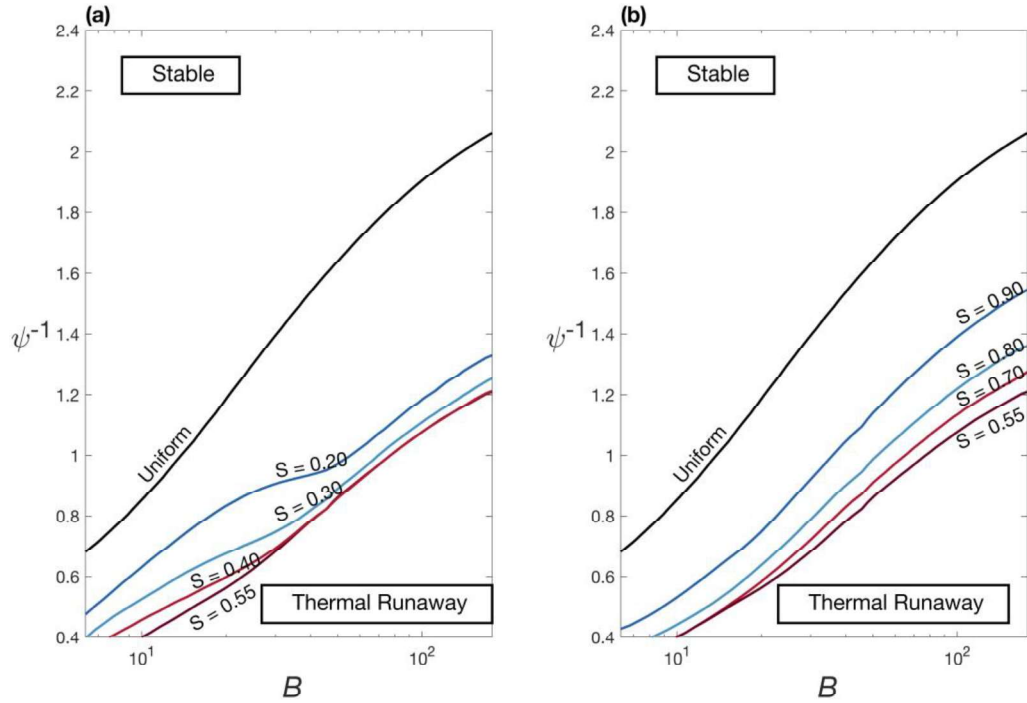


Fig. 10. Locus of maximum distance points to the uniform activity runaway boundary at various step locations S for $\gamma = 10$, $Da = 1$ and $n = 2$. **a:** $S = 0.20$ to 0.55 ; **b:** $S = 0.55$ to 0.90 .

Figs. 10(a) and (b) show the runaway boundaries for a second-order reaction. Particularly at higher B , it can be seen that all the boundaries move downwards when compared to the first-order reaction cases of Figs. 6 and 7. Again $S \approx 0.55$ is the optimal choice, albeit for low B the step location has hardly any effect between $S = 0.5$ and 0.7 . Consequently, under the constraint of Eqn. 7, choosing $S \approx 0.55$ delivers the most potential for benefit, regardless of the parameter values B , Da , γ and n . This means that it is a robust choice of location to split the catalyst activity, even when there is uncertainty in the other parameters, greatly simplifying the problem to the optimization of A_2/A_1 only.

The optimal values of A_2/A_1 (with $S = 0.55$) as a function of B for the sets of dimensionless parameters corresponding to Figs. 6 to 10 are shown in Fig. 11.

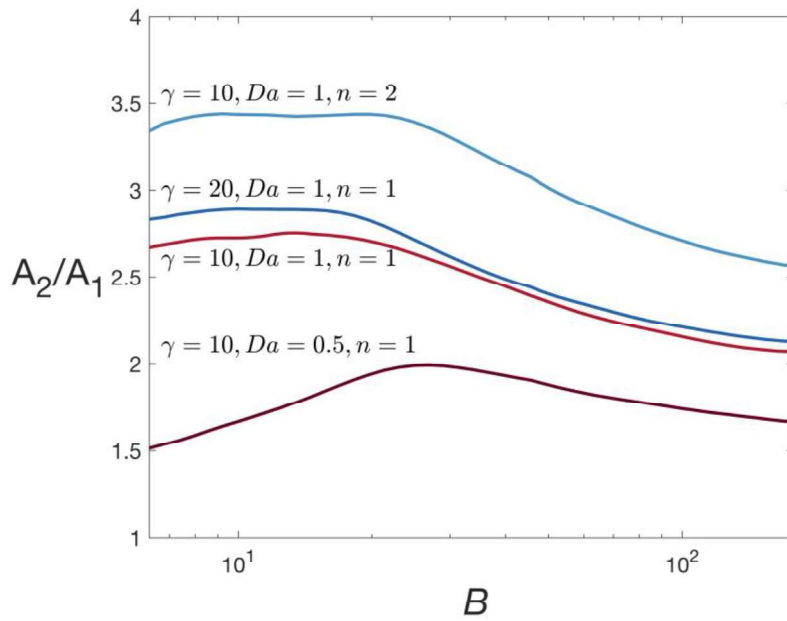


Fig. 11. Optimum values of the activity ratio as a function of B , for different values of γ , Da and n .

3.5 Increased throughput

In the previous section, we showed that stacking of catalyst activity allows for increased conversion and hence increases STY, a key metric for assessing reactor performance [38-41]. STY is defined as the amount of product synthesized per unit volume of catalyst bed per unit of time:

$$STY = \frac{C_{A0}X_A u_0}{L} \quad (9)$$

The inlet concentration C_{A0} is often determined by upstream processes or feedstock characteristics, while the “design conversion X_A ” is typically governed by an economic balance between selectivity, separation and recycle costs, as well as other process specific aspects such as conversion-dependent catalyst decay. For an existing reactor, another way to improve STY is to increase the throughput, i.e. u_0 . Provided the plant downstream can accommodate such an increase, this typically has a significantly higher economic advantage than increased per-pass conversion. Thus, it would be useful to explore how the benefit of stacking could be realized by increasing the throughput parameter u_0 . Consequently, we investigated whether generic guidelines for the configuration of stacked beds could be identified, with the goal of maximizing STY by increasing u_0 whilst keeping the conversion constant.

For a constant heat transfer coefficient U , the location in the classic Barkelew plot is not affected by u_0 because neither ψ^{-1} nor B depend on it. So, by increasing u_0 in reactors with uniform catalyst activity, the hot spot temperature remains constant but shifts towards the reactor’s outlet, and hence the conversion will decrease. In the limit, the hot spot is pushed beyond the reactor length, resulting in PAO.

However, for reactors with stacked catalyst activity, the effects are not as straightforward and may be counterintuitive: increasing u_0 can paradoxically increase conversion because the first hot spot is pushed downstream. This in turn results in less reactant consumption in the first zone and thus a more concentrated reactant enters the higher activity A_2 zone, increasing the rate for positive order reactions. Moreover, as explained in the previous section, a stacked bed may be pushed into thermal runaway when u_0 is increased, owing to the decrease in Da with increasing u_0 . In that case, the runaway boundaries for a stacked bed shift upwards in the Barkelew plot, which can be seen by comparing Figs. 7 and 9.

With this in mind, we explored three strategies to maximize STY by optimizing the stacking configuration, whilst keeping the per pass conversion constant. Each of these strategies starts from the runaway boundary for the uniform bed and then for an arbitrary stacking configuration:

1. increase T_c until thermal runaway is detected in the stacked bed (equivalent to the previous objective of improving conversion alone), then increase u_0 to restore the conversion to that of the uniform bed.
2. increase u_0 until the conversion in the stacked bed is equal to the equivalent reactor with uniform activity.
3. simultaneously increase T_c and u_0 ; upon detecting thermal runaway, decrease T_c to bring conversion back to match the uniform bed.

The first strategy failed in general, as increasing u_0 whilst operating on the runaway boundary for the stacked bed, tended to send the second zone into thermal runaway, for the reasons outlined in section 3.4 (i.e. lowering Da reduces the “shielding effect”). The second strategy was successful for activity profiles with step locations deep into the reactor ($S > 0.60$) combined with values of B lower than around 40, generating an improvement in u_0 of up to 30%. The implication of this in practice is that the throughput of an existing reactor could be significantly increased, by stacking activities, whilst still maintaining the same single-pass conversion as the uniform bed. The third strategy was also feasible, generating a similar improvement in u_0 of up to 30%. In this case, increasing T_c at the same time as u_0 consumed the margin available for further increase u_0 in throughput, with the improvement in STY being comparable to the second strategy.

A significant increase in u_0 was most feasible at low B , in the region of PAO. It appeared from this work that catalyst activity profiles, which produced PAO in the first zone, were most amenable to increasing u_0 . Overall, although some benefits to STY were realized, we were unable to identify generic guidelines for the configuration of a stacked bed, with the objective of maximizing STY.

Visualizing the regions of PAO and HSO may reveal generic guidelines for maximizing STY, similar to those found for maximizing conversion.

3.6 Catalyst dilution

In the previous sections, the total activity in the stacked bed was forced to be the same as in the equivalent uniform bed. Thus, a decrease in activity in the first zone must then be compensated by an increase in the second zone, according to Eqn. (7). Although this was an artificial constraint, it enabled an equitable comparison between the performance of a particular reactor with uniform catalyst activity, and with two zones of different activity. In addition, it ensured that the value of Da for the uniform bed retained some relevance to the stacked one.

However, for an existing commercial scale process, the catalyst activity is typically optimized by taking into account selectivity and catalyst deactivation. Often the option to have a catalyst with activity $A_2 > 1$ is either not realistic or would require significant catalyst R&D; typically increasing the activity of a commercialized catalyst can only be achieved easily at the cost of some selectivity loss. Therefore, in this section we consider the case where heat production in the upstream section of the reactor is suppressed by diluting the first bed with inert particles (or by dilution of the active phase within the catalyst particle itself). In this case, Eqn. (7) is replaced by $A_1 < 1$ and $A_2 = 1$. Adopting the same methodology as before, we can thus define a specific catalyst activity profile representing bed dilution in the first zone and compute its thermal runaway boundaries.

Fig. 12 shows the phase diagram when $S = 0.25$, $A_1 = 0.625$ and $A_2 = 1$ (i.e. $A_2/A_1 = 1.60$), using the same default dimensionless parameters as before. It closely resembles the Type II behavior in Fig. 3, both in terms of the position of the runaway boundaries and the temperature profiles in each region. Thus, removing the constraint on total activity in the stacked bed does not appear to qualitatively affect the phase diagram. However, with catalyst dilution, the optimal conversion improvement at lower values of B decreases from 7.1% to 4.8%, and from 4.6% to 2.1% at higher values, compared to the constant total activity case in Fig. 5.

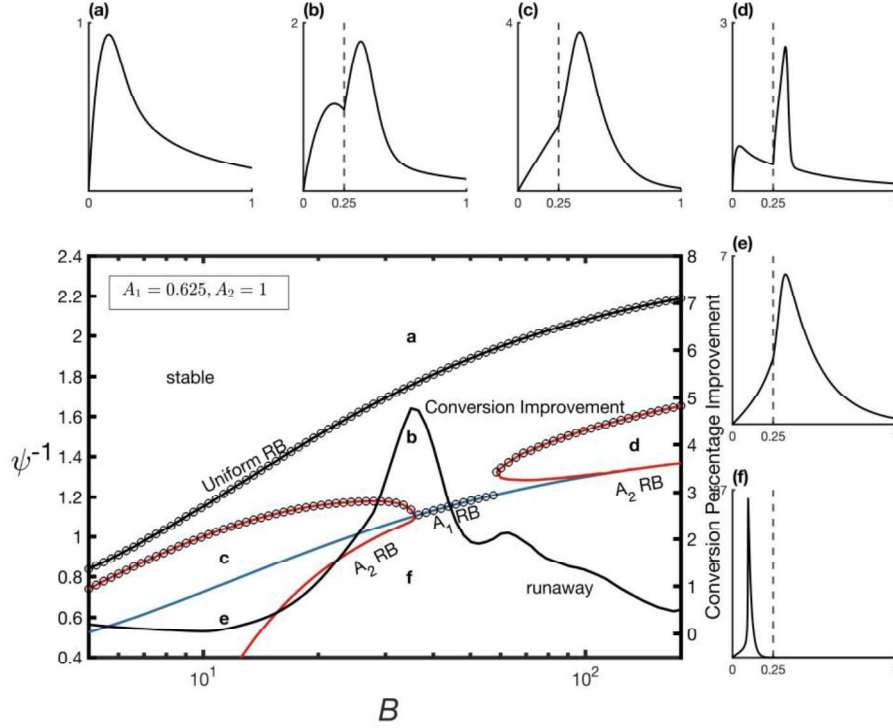


Fig. 12. Runaway boundary plot at $n = 1$, $Da = 1$, $\gamma = 10$ for catalyst activity profile $A_1 = 0.625$ and $A_2 = 1$, with associated temperature profile examples. Lines highlighted with circles denote stable operating points. RB = Runaway Boundary; **a** safe operation under uniform activity profile with $B = 20$ and $St = 40$; **b** safe operation under stacked activity profile with $B = 20$ and $St = 26$; **c** thermal runaway in the second zone under stacked activity profile with $B = 10$ and $St = 8$; **d** thermal runaway in the second zone under stacked activity profile with $B = 120$ and $St = 200$; **e** thermal runaways in both zones under stacked activity profile with $B = 10$ and $St = 5$; **f** thermal runaway in the first zone under stacked activity profile with $B = 50$ and $St = 55$.

4 Conclusions and future work

For any arbitrary (non-optimized) stacking configuration we identified three distinct types of modified Barkedew plots, or “phase diagrams”. These diagrams quantitatively show the improvement via a vertical shift in the runaway boundary compared to the uniform activity case. The intersection points in such a phase diagram correspond to a combination of activity ratio and step location where there is simultaneously an inflection point before the first and before the second hot spot, i.e. both hot spots are equally limiting. Out of the three distinct types of phase diagrams, only with a Type II stacking configuration can this occur. Therefore, we concluded that this special feature can be fruitfully exploited to develop a first optimization criterion for the selection of the activity ratio and step location to maximize conversion and, or STY.

An alternative optimization criterion is based on maximizing the vertical separation between the uniform activity and stacked activity runaway boundaries. We showed that these two criteria are virtually equivalent by comparing their corresponding conversion improvements. Applying both optimization criteria yielded the optimal combination of the step location S and the activity ratio A_2/A_1 as a function of the dimensionless heat generation potential parameter B . Rather surprisingly, this led to the conclusion that an activity step location around $S = 0.55$ consistently provides the greatest, or very close to the greatest, separation from the uniform activity boundary i.e. offering the highest improvement in thermal stability, provided the corresponding (and B dependent) value of A_2/A_1 is applied. This value of $S \approx 0.55$, i.e. just after the middle of the bed, is virtually independent of the value of B and any of the other dimensionless groups. Tentatively, we conclude that this finding may be exploited in future work allowing for more than two catalyst activities in the reactor.

Of course, many practical aspects must be considered before implementing stacking of catalysts at an industrial scale, for example: the more cumbersome loading of the sometimes $> 10,000$ tubes in an MTR; can one actually make a catalyst with significantly different activities without affecting other properties like selectivity or catalyst stability; and what is the effect of deactivation of the catalyst, including non-uniform deactivation with the axial position in the tube? These aspects would need to be addressed on a case-by-case basis.

We recommend further work on maximizing space-time yield (STY) by increasing throughput rather than (per pass) conversion as a quasi-economic objective function, thus exploiting the improved stability via increased throughput. In our opinion this requires a solution to the complications we identified, such as the effect of increased u_0 on the Damköhler number and that it suppresses the identified shielding effect. We suggest extending the analysis of pseudo-adiabatic operation (PAO) and hot spot operation (HSO) regions to fully capitalize on the insights offered by our current study. Further extensions may comprise alternative activity profiling constraints (e.g. allowing more than two zones of activity), incorporating the effect of particle scale heat transfer as done by Balakotaiah and Luss [36] and introducing a “margin to runaway” in the assessment of the benefit of stacking in practice.

In conclusion, our analysis so far demonstrates the potential of catalyst activity stacking to improve the conversion and, or productivity of an MTR in a generalized way, providing a more holistic understanding of thermal runaway in the case of stacked beds of catalysts.

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Declaration of competing interest

The authors declare that there are no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. The dimensional model equations and numerical procedures

The classic steady-state one-dimensional pseudo-homogeneous plug flow model equations for an n th-order irreversible reaction in a wall cooled catalytic tubular reactor are:

$$\frac{du_0 C_A}{dz} = -A \rho_b k_0 \exp\left(-\frac{E_a}{RT}\right) C_A^n \quad (A.1)$$

$$C_A(z = 0) = C_{A,0}.$$

$$u_0 \rho c_p \frac{dT}{dz} = A \rho_b k_0 \exp\left(-\frac{E_a}{RT}\right) C_A^n (-\Delta H_R) - \frac{4U}{d_t} (T - T_c) \quad (A.2)$$

$$T(z = 0) = T_0 = T_c$$

Note that for simplicity, like previous authors in the field of thermal stability in tubular reactors, the fluid velocity (i.e. the gas density) must be assumed constant to obtain the concise

dimensionless Eqns. (1-3). Especially in the case of multiple reactions this may give rise to significant errors $\gg 5\%$ even for density variations $< 5\%$, see Bos and Westerterp [42] who recommended to never apply this simplification. However, for the current study, the heat balance is dominant, and $u_0\rho$ is constant regardless of the change in velocity due axial changes in temperature or mean molar mass.

To render the equations dimensionless, we follow e.g. Wu et al. [37] and define:

$$X_A = \frac{C_{A,0} - C_A}{C_{A,0}} \quad (\text{A.3})$$

$$Z = \frac{z}{L} \text{ and } \theta = \frac{T - T_c}{T_c} \frac{E_a}{RT_c} \quad (\text{A.4})$$

All the runaway boundaries and Barkelew plots in this work are generated by the following procedure and pseudo-code:

1. For a fixed set of parameters n , γ and Da , and activity profile A_2/A_1 and S : calculate A_1 and A_2 from Eqn. (7)
2. Start from $B = 5$; use $St = 600$ as an initial guess
3. Solve Eqn. (1) and (2) with the given n , γ , Da , A_1 , A_2 , S , B and St , subject to the boundary conditions in Eqn. (3)
4. Check whether the system is in thermal runaway using the runaway criterion of Eqn. (6):
 - a. If not in thermal runaway, decrease the value of St by 1 and repeat steps 3 and 4
 - b. If in thermal runaway, increase the value of St by 0.99
 - c. Repeat step 3 and check whether the system is in thermal runaway using the runaway criterion of Eqn. (6):
 - i. If not in thermal runaway, decrease the value of St by 0.01 and repeat step 4.c
 - ii. If in thermal runaway, increase the value of St by 0.01. This is the critical St corresponding to $B = 5$. The values of St and B can be used to find the

critical ψ^{-1} using Eqn. (4). Break the loop of decreasing St and proceed to step 5

5. Repeat steps 2 to 4 for various values of B and find the array of critical values of ψ^{-1} corresponding to these B values
6. Plot ψ^{-1} against B , which yields the Barkelew plot based on Dente & Collina's runaway criterion.

Step 4a may take multiple loops to converge starting from the large St value of 600. For instance, consider B is 10 and its corresponding critical St is 12, then it will take 589 loops before St arrives at 12. Thus, for smaller B values (< 50), St can be initialized at smaller values (< 100) to increase the computation speed. Moreover, steps 4.b and 4.c are designed to improve the numerical accuracy from 10^0 to 10^{-2} , leading to more smoother lines in the Barkelew plots.

The primary software used in this investigation was MATLAB R2023b, and the simulations were carried out on a desktop with a 3.1 GHz Dual-Core Intel Core i5 processor. Since none of the solution profile plots (e.g. temperature, conversion) was expected to display significant variations over an unacceptably small reactor segment outside thermal runaway regions, the problem to be investigated was non-stiff. Thus, the suitable ODE solver in MATLAB was ode45, which was based on an explicit Runge-Kutta formula, the Dormand-Prince pair [43].

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