

Research Article

The Effects of Mixing, Reaction Rates, and Stoichiometry on Yield for Mixing Sensitive Reactions—Part II: Design Protocols

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Competitive-consecutive and competitive-parallel reactions are both mixing sensitive reactions where the yield of desired product depends on how fast the reactants are brought together. Recent experimental results have suggested that the magnitude of the mixing effect may depend strongly on the stoichiometry of the reactions. To investigate this, a 1D, dimensionless, reaction-diffusion model was developed at the micromixing scale, yielding a single general Damköhler number. Dimensionless reaction rate ratios were derived for both reaction schemes. A detailed investigation of the effects of initial mixing condition (striation thickness), dimensionless reaction rate ratio, and reaction stoichiometry on the yield of desired product showed that the stoichiometry has a considerable effect on yield. All three variables were found to interact strongly. Model results for 12 stoichiometries are used to determine the mixing scale and relative rate ratio needed to achieve a specified yield for each reaction scheme. The results show that all three variables need to be considered when specifying reactors for mixing sensitive reactions.

1. Introduction

Mixing-sensitive reactions are reactions which are particularly sensitive to the rate at which the reactants are brought together, that is, how fast they are mixed. These reactions are of two main types: the competitive-consecutive (C-C) reaction scheme, which involves two competing reactions where the second unwanted reaction consumes the desired product from the first reaction, and the competitive-parallel (C-P) reaction scheme, where two reactions compete for a limiting reagent, forming a desired and undesired product. The effects of mixing and relative reaction rates of the competing reactions have been investigated previously and it is known that mixing can affect the product distribution significantly. Past work has concentrated on the investigation of a single classical stoichiometry for each of the reaction schemes [1–25]. This work investigates whether the

stoichiometry of the reaction plays a role in determining the maximum final yield of desired product and how the three reactor design variables—mixing, reaction, rate and stoichiometry interact.

In a previous paper by Shah et al. [26], a model was developed to capture the effects of reaction stoichiometry, mixing, (characterized by the Damköhler number (Da)), and relative reaction rates, (characterized by a dimensionless reaction rate ratio (k_2/k_1)). General forms of the reactions as given in Table 1 were used to derive mass balance equations. From the equations a single Damköhler number that is common to both reaction types and all stoichiometries (Da) and a dimensionless reaction rate ratio (k_2/k_1) that is specific to each reaction type were obtained. Both Da and k_2/k_1 depend on the stoichiometric coefficients of the reaction scheme, making the potential impact of stoichiometry immediately

evident. The expression for the general Damköhler number is:

$$\begin{aligned} \text{Da} &= k_1' \left(\frac{\rho_T}{M} \right)^\epsilon \frac{L_B^2}{D_B} = \frac{k_1' (\rho_T/M)^\epsilon}{(D_B/L_B^2)} \\ &= \frac{\text{rate of desired reaction}}{\text{rate of diffusion}} \\ &= (\text{rate of desired reaction}) * (\text{diffusion time}). \end{aligned} \quad (1)$$

The effect of stoichiometry on the Damköhler number is given by ϵ , the stoichiometric coefficient of the limiting reagent (B) in the desired reaction. The diffusion time in the smallest eddies is determined by the mixing scale, L_B , the thickness of the smallest striation of concentration homogeneity, and the molecular diffusivity, D_B , which completes the variables needed to determine the diffusion time at the smallest scales of segregation.

The effect of the relative reaction rates of the competing reactions is also of interest. The model provides dimensionless reaction rate ratios for the C-C and C-P reactions as follows:

$$\text{C-C: } \frac{k_2}{k_1} = \left[\frac{\beta}{\alpha} \left(\frac{\alpha}{1+\epsilon} \right)^\beta \left(\frac{\rho_T}{M} \right)^{\beta+\gamma-\epsilon-1} \right] \frac{k_2'}{k_1'}, \quad (2)$$

$$\text{C-P: } \frac{k_2}{k_1} = \left[\frac{\gamma}{\epsilon} \left(\frac{\rho_T}{M} \right)^{\gamma-\epsilon} \right] \frac{k_2'}{k_1'}. \quad (3)$$

These dimensionless reaction rate ratios are specific to the type of mixing sensitive reaction, C-C or C-P, and incorporate the effect of the relative reaction rates of the competing reactions (k_2'/k_1') as well as the effect of stoichiometry. The model was validated for the classical reaction stoichiometry where all coefficients are equal to 1. This work extends the simulations to ten new stoichiometries where one or more of the coefficients are greater than one.

For both the C-C and C-P simulations, the Damköhler number was varied from 0.01 to 10 000 in 100x increments, where 0.01 is the best and 10 000 is the worst mixing. The dimensionless reaction rate ratio (k_2/k_1) was varied from 1 to 0.00001 in 10x increments, where 1 is the worst ratio and 0.00001 is the best ratio. For the C-C reactions, ϵ was always 1 and α, β, γ were given a value of either 1 or 2. For the C-P reactions, ϵ and γ were either 1 or 2. Table 2 shows the different C-C reaction scheme stoichiometries investigated, with the corresponding dimensionless reaction rate ratios. Table 3 shows the same terms for the C-P reaction schemes.

We caution the reader that this model is highly simplified. Elementary reactions involving 4 molecules do not exist, so the kinetic expressions for Cases 7 and 8 for the C-C reaction schemes and for Case 4 for the C-P reactions will assuredly have a different and more complex form for real reactions with similar stoichiometries. The mixing model is equally flawed when considering real systems. The simple striation model does not allow for variation of striation thickness with time as mixing progresses or between eddies; it includes no consideration of the effects of stretching and no mixing between layers. The dynamics of a more realistic model of

TABLE 1: General mixing sensitive reaction schemes.

Competitive consecutive (C-C)	Competitive parallel (C-P)
$A + \epsilon B \xrightarrow{k_1'} \alpha P$	$A + \epsilon B \xrightarrow{k_1'} P$
$\beta P + \gamma B \xrightarrow{k_2'} S$	$C + \gamma B \xrightarrow{k_2'} S$

turbulence would be much more complex. Keeping these limitations in mind, the goal of this work is to investigate whether a hypothesis that the reaction stoichiometry can have a significant impact on the course of mixing sensitive reactions is reasonable.

2. Numerical Details

Simulation of the systems of five or six PDEs for the C-C and C-P reaction schemes, respectively (shown in Tables 4 and 5), was carried out using COMSOL 3.4, a finite element PDE Solver. It is worth noting that for the C-C reaction scheme only four of the equations are independent while for the C-P reaction scheme there are five independent equations. The 1D, transient, convection, and diffusion mass transport model was used, with the mass fractions for each species specified as the independent variables. The default Lagrangian-quadratic element was chosen. The specified 1D geometry line of unit length was split equally into two subdomains and a mesh of 2048 equally spaced elements with 2049 nodes was generated. The mesh was tested for grid independence, and it was found that 1024 elements was sufficient resolution to ensure repeatable results to within the required tolerance of the solver, which was set to 10^{-6} . Since the geometry was only 1D and the computational cost was minimal, a finer mesh than the minimum required resolution was used. The total time taken per simulation was approximately 30 seconds. The boundary conditions were specified for no net mass transfer across the boundaries.

Figure 1 shows the initial conditions for the C-C and C-P schemes. For the C-C cases, the initial conditions were chosen such that all of the mass initially present could be converted to desired product P . This was done by specifying a ratio of $A : B$ as 1 : 1 in all the simulations, with A and B being present in pure striations, $w_{A_0} = w_{B_0} = 1$. For the C-P scheme, owing to the parallel nature of the reactions, the initial conditions were a bit more complicated. They were chosen such that either A or C could consume the entire limiting reagent B by themselves, that is, the initial ratios depended on the stoichiometric coefficients in the reaction scheme. In order to satisfy the constant mass concentration assumption of the model, it was necessary to include the inert in the C-P simulations. w_{B_0} and w_{I_0} were always set to 0.5, and $w_{A_0} w_{C_0}, w_{Y_0}$ were calculated accordingly.

For most cases the limiting reagent, B , was completely consumed by $\text{Da} \cdot t^* = 500$ so the transient simulation results are shown from $\text{Da} \cdot t^* = 0$ to $\text{Da} \cdot t^* = 500$. $\text{Da} \cdot t^*$ is equivalent to a dimensionless reaction time where $\text{Da} \cdot t^* = t/\tau_R$, so running all simulations to $\text{Da} \cdot t^* = 500$ is the same as running all simulations for 500 reaction times.

TABLE 2: Stoichiometries of reaction schemes and the corresponding dimensionless reaction rate ratio for the eight different C-C reactions. Da was always $Da = k'_1(\rho_T/M)(L_B^2/D_B)$.

Case	Reaction scheme	$\epsilon, \alpha, \beta, \gamma$	k_2/k_1
1	$A + B \xrightarrow{k'_1} 2P$ $P + B \xrightarrow{k'_2} S$	1, 2, 1, 1	$(1/2)(k'_2/k'_1)$
2	$A + B \xrightarrow{k'_1} P$ $P + B \xrightarrow{k'_2} S$	1, 1, 1, 1	$(1/2)(k'_2/k'_1)$
3	$A + B \xrightarrow{k'_1} P$ $2P + B \xrightarrow{k'_2} S$	1, 1, 2, 1	$(1/2)(\rho_T/M)(k'_2/k'_1)$
4	$A + B \xrightarrow{k'_1} 2P$ $2P + B \xrightarrow{k'_2} S$	1, 2, 2, 1	$(\rho_T/M)(k'_2/k'_1)$
5	$A + B \xrightarrow{k'_1} 2P$ $P + 2B \xrightarrow{k'_2} S$	1, 2, 1, 2	$(1/2)(\rho_T/M)(k'_2/k'_1)$
6	$A + B \xrightarrow{k'_1} P$ $P + 2B \xrightarrow{k'_2} S$	1, 1, 1, 2	$(1/2)(\rho_T/M)(k'_2/k'_1)$
7	$A + B \xrightarrow{k'_1} P$ $2P + 2B \xrightarrow{k'_2} S$	1, 1, 2, 2	$(1/2)(\rho_T/M)^2(k'_2/k'_1)$
8	$A + B \xrightarrow{k'_1} 2P$ $2P + 2B \xrightarrow{k'_2} S$	1, 2, 2, 2	$(\rho_T/M)^2(k'_2/k'_1)$

TABLE 3: Stoichiometries of reaction schemes and the corresponding dimensionless reaction rate ratio and Damköhler number for the four different C-P reactions.

Case	Reaction scheme	ϵ, γ	k_2/k_1	Da
1	$A + B \xrightarrow{k'_1} P$ $C + B \xrightarrow{k'_2} S$	1, 1	k'_2/k'_1	$k'_1(\rho_T/M)(L_B^2/D_B)$
2	$A + B \xrightarrow{k'_1} P$ $C + 2B \xrightarrow{k'_2} S$	1, 2	$2(\rho_T/M)(k'_2/k'_1)$	$k'_1(\rho_T/M)(L_B^2/D_B)$
3	$A + 2B \xrightarrow{k'_1} P$ $C + B \xrightarrow{k'_2} S$	2, 1	$(1/2)(\rho_T/M)^{-1}(k'_2/k'_1)$	$k'_1(\rho_T/M)^2(L_B^2/D_B)$
4	$A + 2B \xrightarrow{k'_1} P$ $C + 2B \xrightarrow{k'_2} S$	2, 2	k'_2/k'_1	$k'_1(\rho_T/M)^2(L_B^2/D_B)$

The modelled equations allow for specification of the Damköhler number, the dimensionless reaction rate ratio and the stoichiometry. All possible combinations of the values of reaction rate ratio, Damköhler number, and stoichiometry for the C-C reaction scheme (stoichiometries given in Table 2) and the C-P reaction scheme (stoichiometries given in Table 3) were investigated. This resulted in 192 converged cases for the C-C and 96 converged cases for the C-P reaction scheme.

3. Results and Discussion

The results obtained for the simulations are profiles of mass fraction for each of the species over the space x^* for all dimensionless times t^* . Samples of these results were given in Shah et al. [26] (Figures 2 and 3, resp.).

Since the main process objective is to maximize the production of desired product P , the profiles of mass fraction of P are of most interest. These profiles were integrated over the domain to obtain the total mass of desired product and the instantaneous yield using the formula:

$$Y_P = \frac{\text{mass of species } P \text{ at } t^*}{\text{max mass of } P \text{ obtainable}} = \frac{\int_{-0.5}^{0.5} w_P dx^*(t^*)}{0.5w_{B_0}(1 + 1/\epsilon)}. \quad (4)$$

Following Y_P over time gives the progression of yield over time. The total production of P as time progresses can be observed in a plot of Y_P versus dimensionless time $Da \cdot t^*$. Figures 4 and 5 in Shah et al. [26] show examples of such plots.

The final yield of P at $Da \cdot t^* = 500$ was plotted against Da and k_2/k_1 to assess the effects of each of the variables on the final yield of desired product. Representative figures are presented here. The results (Y_P versus Da and k_2/k_1)

TABLE 4: System of equations for competitive-consecutive reaction scheme, to be used with (1) and (2).

Species	Mass balance partial differential equation
A	$\partial(w_A)/\partial t^* = \left(\partial^2(w_A)/\partial x^{*2}\right) - [Da w_A w_B^\epsilon]$
B	$\partial(w_B)/\partial t^* = \left(\partial^2(w_B)/\partial x^{*2}\right) - \epsilon [Da w_A w_B^\epsilon] - (\alpha\gamma/\beta) \left[Da(k_2/k_1)w_P^\beta w_B^\gamma\right]$
P	$\partial(w_P)/\partial t^* = \left(\partial^2(w_P)/\partial x^{*2}\right) + (1 + \epsilon) \left[Da w_A w_B^\epsilon - Da(k_2/k_1)w_P^\beta w_B^\gamma\right]$
S	$\partial(w_S)/\partial t^* = \left(\partial^2(w_S)/\partial x^{*2}\right) + (1 + \epsilon + (\alpha\gamma/\beta)) \left[Da(k_2/k_1)w_P^\beta w_B^\gamma\right]$
I	$\partial(w_I)/\partial t^* = \partial^2(w_I)/\partial x^{*2}$

TABLE 5: System of equations for competitive-parallel reaction scheme, to be used with (1) and (3).

Species	Mass balance partial differential equation
A	$\partial(w_A)/\partial t^* = \left(\partial^2(w_A)/\partial x^{*2}\right) - [Da w_A w_B^\epsilon]$
B	$\partial(w_B)/\partial t^* = \left(\partial^2(w_B)/\partial x^{*2}\right) - \epsilon [Da w_A w_B^\epsilon] - \epsilon \left[Da(k_2/k_1)w_C w_B^\gamma\right]$
C	$\partial(w_C)/\partial t^* = \left(\partial^2(w_C)/\partial x^{*2}\right) - (\epsilon/\gamma) \left[Da(k_2/k_1)w_C w_B^\gamma\right]$
P	$\partial(w_P)/\partial t^* = \left(\partial^2(w_P)/\partial x^{*2}\right) + (1 + \epsilon) [Da w_A w_B^\epsilon]$
S	$\partial(w_S)/\partial t^* = \left(\partial^2(w_S)/\partial x^{*2}\right) + (\epsilon + (\epsilon/\gamma)) \left[Da(k_2/k_1)w_C w_B^\gamma\right]$
I	$\partial(w_I)/\partial t^* = \partial^2(w_I)/\partial x^{*2}$

make up a 3D surface for each stoichiometry. Slices of the results are presented as follows: a base case set of six slices of Y_P versus Da is presented to show the effects of mixing (Da) and dimensionless reaction rate ratio (k_2/k_1) on yield of desired product. Where a point needs to be clarified, the results are replotted by taking a slice along the k_2/k_1 axis or by expanding the time variable. The results are then revisited to focus on the effect of stoichiometry and how it interacts with mixing and reaction rate. The same set of plots is repeated for the C-P reaction schemes. The results are then summarized to show a possible design specification space of Da and k_2/k_1 for a specified yield.

3.1. Competitive-Consecutive (C-C) Reaction. Figures 2(a) to 2(f) are semilog plots of the final Y_P versus Damköhler number for decreasing dimensionless reaction rate ratio, k_2/k_1 . The curves on each of the plots represent the eight C-C stoichiometry cases. The effects that are of interest are the effects of the Damköhler number (mixing), reaction rate ratio k_2/k_1 (chemical kinetics), and the reaction stoichiometry (Cases 1 to 8). The Damköhler number is plotted on the x -axis and the results are first presented from this perspective. Next, the effect of ratio k_2/k_1 is observed by comparing graphs (a) to (f). Finally the effect of stoichiometry (Cases 1 to 8) within each graph is reviewed and summarized. At each step, selected results are replotted either to illustrate a point more clearly or to provide a perspective on the data.

3.1.1. The Effect of Damköhler Number (Da): The Well-Mixed Limit. The plots in Figure 2 show a decrease in yield of desired product with increasing Damköhler number. This trend is true for all stoichiometries and at all values of k_2/k_1 . A larger Damköhler number represents worse mixing (larger striations) and a smaller Damköhler number represents improved mixing (smaller striations). The yield for $Da = 1$ and $Da = 0.01$ is the same for all stoichiometries at all

k_2/k_1 . The yield at $Da = 100$ decreases for the cases with unfavourable dimensionless reaction rate ratios ($k_2/k_1 \geq 0.01$) but remains for same for the favourable k_2/k_1 ratios ($k_2/k_1 \leq 0.001$). By $Da = 10000$ the yield always decreases, regardless of the value of k_2/k_1 .

The data is replotted in Figures 3(a) and 3(b) for the best (Case 7) and worst (Case 2) stoichiometry cases to confirm the Y_P versus k_2/k_1 trends. This shows that the results for $Da = 0.01$ and $Da = 1$ lie exactly on top of one another. When Da is increased from 1 to 100 the curves diverge over part of the domain: for Case 2 when $k_2/k_1 \geq 0.001$ and for Case 7 when $k_2/k_1 \geq 0.01$. It is concluded that $Da = 1$ is the well-mixed limit for large k_2/k_1 , while $Da = 100$ is the well-mixed limit for small k_2/k_1 and that the meaning of “large k_2/k_1 ” depends on the stoichiometry.

3.1.2. The Effect of Dimensionless Reaction Rate Ratio (k_2/k_1): Can Chemistry Solve the Problem? Looking at the changes in Figure 2 from (a) to (f), as k_2/k_1 decreases the yield increases. This result is as expected, since a smaller k_2/k_1 gives a slower undesired side reaction. As k_2/k_1 is decreased it is also clear that the curves for the different stoichiometric cases approach, collapsing onto one curve by $k_2/k_1 = 0.0001$. The results are replotted to directly compare the effect of k_2/k_1 on the 8 cases in Figure 4(a): $Da = 1$ (well mixed), (b) $Da = 100$ and (c) $Da = 10000$ (badly mixed).

Y_P increases to 1 as k_2/k_1 decreases for all stoichiometries, with the 8 cases collapsing at about $k_2/k_1 = 0.001$ for the well-mixed cases and at $k_2/k_1 = 0.0001$ for $Da = 10000$, the badly mixed case. The yield of the badly mixed case is about half of what was obtained in the well-mixed results. This brings up an interesting question: “Is it possible to get perfect yield of desired product, that is, $Y_P \sim 1$, for $Da = 10000$, a badly mixed case?” The simulations for the $Da = 10000$ cases were rerun for a hundred times longer to $Da \cdot t^* = 50000$ instead of $Da \cdot t^* = 500$. Figure 5 shows the results of these simulations. To obtain a perfect yield with

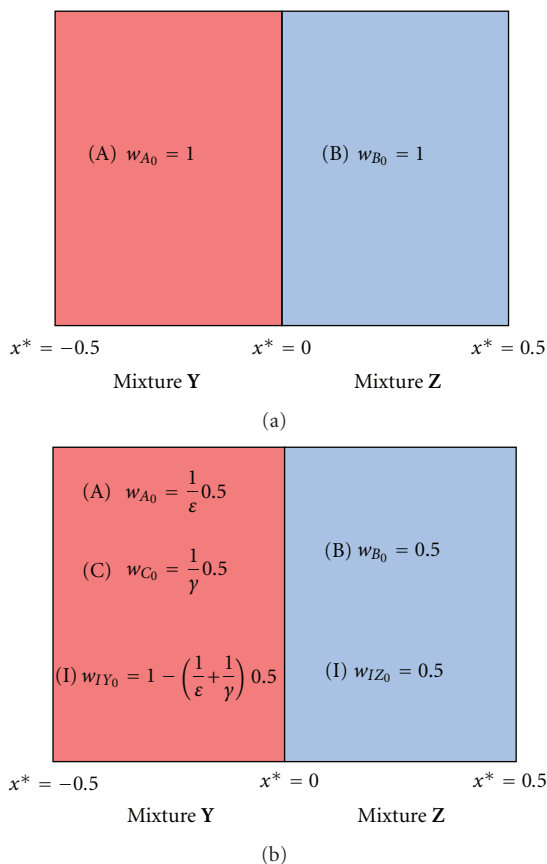


FIGURE 1: Initial conditions for (a) C-C and (b) C-P reaction scheme simulations.

insufficient mixing, both a 100x longer reaction time and 100x better chemistry are required. This clearly illustrates the need for an improved understanding of mixing.

3.1.3. Effect of Stoichiometry. Returning for a final time to Figure 2 there is a clear effect of stoichiometry on the final yield of desired product, and the effect of stoichiometry shows interactions with both the mixing scale and the dimensionless reaction rate ratio.

In Figure 2(a) ($k_2/k_1 = 1$) the curves are widely separated, coming closer together as Da increases and the effect of bad mixing becomes dominant. There is a clear distinction between stoichiometries, with Cases 7 and 8 having the highest yields and therefore the most favourable stoichiometry, and Cases 1 and 2 having the lowest yields, meaning they have the least favourable stoichiometries. Cases 1 and 2 require only two molecules for the side reaction, while Cases 7 and 8 require four molecules. This places a mass transfer and collision probability limitation on the side reaction for Cases 7 and 8, hence making them more favourable for the desired reaction. Cases 3–6 all consume 3 molecules in the undesired reaction, making the mass transfer limit similar; however, at the large values of k_2/k_1 , Cases 3 and 4 have a much lower yield of P than Cases 5 and 6, forming two bands.

Comparing the stoichiometries of Cases 1–4 with Cases 5–8, for the first 4 cases, 1 molecule of B is consumed in the second reaction, and in the last 4, 2 molecules of B are consumed. Comparing Case 3 to Case 6 and Case 4 to Case 5, the desired reactions are identical, whereas the stoichiometric coefficients on the undesired reaction are different. Of particular interest is the larger stoichiometric coefficient on reagent B in Cases 5 and 6. An examination of the local concentration profiles showed that B is the limiting reagent locally in the second reaction. Since Cases 5 and 6 require two molecules of the limiting reagent in the undesired reaction, making it harder for the reaction to proceed, it makes sense that the yield of P will be higher for Cases 5 and 6 as compared to Cases 3 and 4.

Now comparing the stoichiometries within pairs, in three of the four pairs producing more P in the first reactions leads to an increase in P consumption in the second reaction and a drop in yield. In other words, at large k ratios, the two reactions compete effectively for reagents. Under these conditions, when less P is produced in the desired reaction, the side reaction is slowed down. The trend is reversed for Cases 3 and 4. These are the only cases where more P is consumed than B in the undesired reaction, so in this case it appears that the mass transfer limit on P relative to B overwhelms the effect of producing more P .

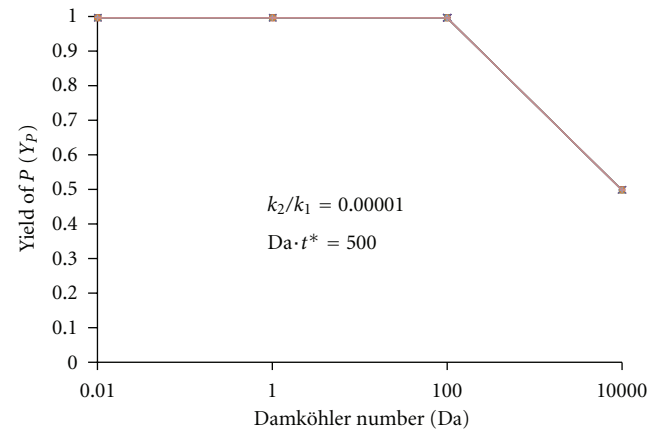
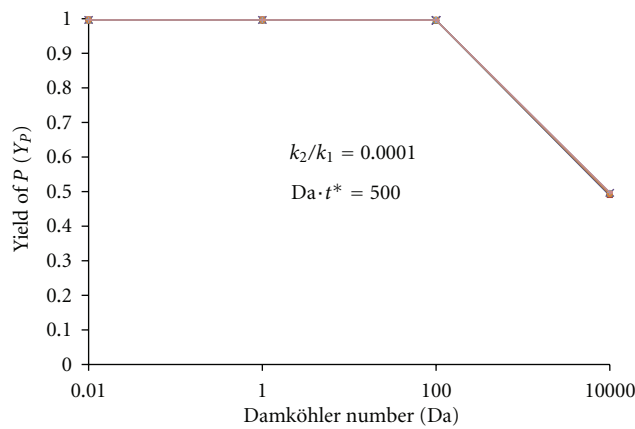
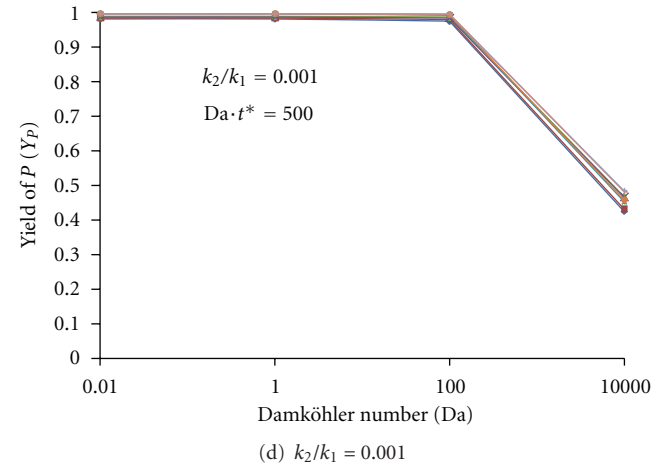
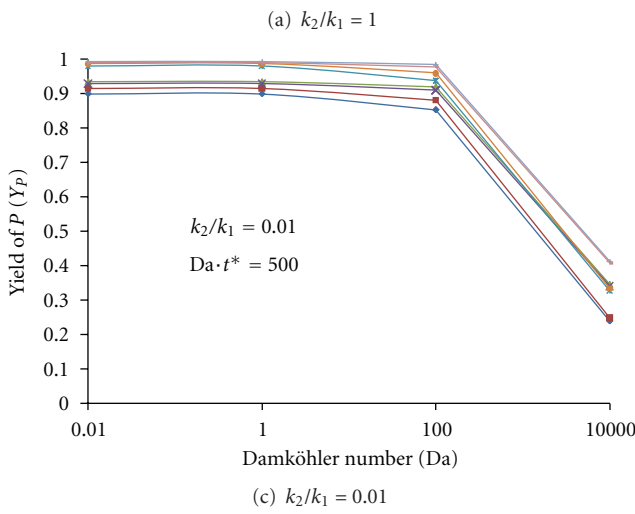
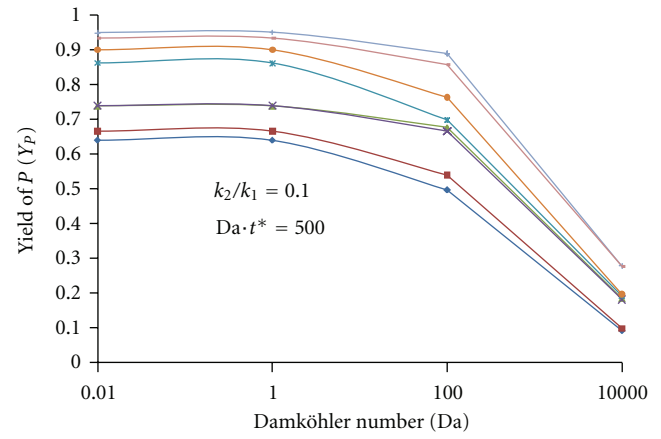
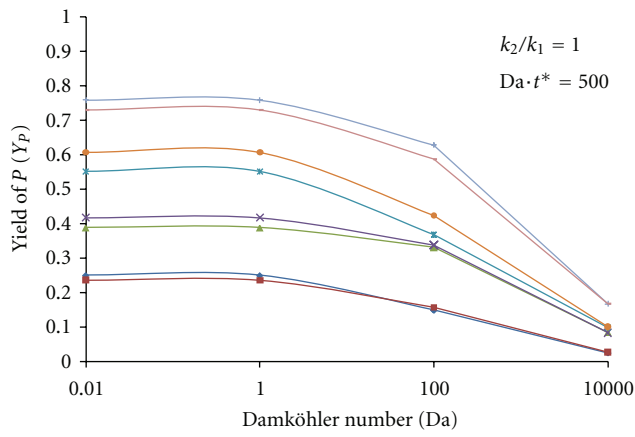
These trends continue in Figure 2(b) ($k_2/k_1 = 0.1$) and Figure 2(c) ($k_2/k_1 = 0.01$). For $k_2/k_1 \leq 0.001$ the curves collapse onto each other and the effect of stoichiometry vanishes. For the very bad mixing condition ($Da = 10000$) that was allowed to proceed for a very long time, Figure 5, the effect of stoichiometry creeps back into the picture, affecting yield at all the way to $k_2/k_1 = 0.00001$.

3.1.4. Summary of Results for the C-C Reaction Scheme. For competitive-consecutive reactions, we have the following.

- $Da \leq 1$ is the well-mixed limit when $k_2/k_1 \geq 0.01$ and $Da \leq 100$ is the limit when $k_2/k_1 < 0.01$.
- $k_2/k_1 \leq 0.001$ with $Da \leq 100$ provides yields $>95\%$ at $Da \cdot t^* = 500$.
- The effect of stoichiometry can be large if the k_2/k_1 is unfavourable. This effect vanishes at $k_2/k_1 \leq 0.001$ for short reaction times and good mixing. At longer reaction times with bad mixing conditions, the effect of stoichiometry reappears and requires a much smaller value of k_2/k_1 to eradicate.
- The most favorable stoichiometry is one where the desired reaction consumes fewer molecules than the undesired reaction, thus placing a mass transfer limitation on the undesired reaction.

3.2. Competitive-Parallel (C-P) Reaction. The analysis proceeds through the same questions posed for the C-C reaction.

- What is the well mixed limit (Da)?
- How much can chemistry contribute (k_2/k_1)?
- Is the stoichiometry important?



- Case 1
- Case 2
- Case 3
- Case 4

(e) $k_2/k_1 = 0.0001$

(f) $k_2/k_1 = 0.00001$

- Case 5
- Case 6
- Case 7
- Case 8

(e) $k_2/k_1 = 0.0001$

(f) $k_2/k_1 = 0.00001$

FIGURE 2: Plots of yield of P versus Da for decreasing k_2/k_1 ratios for the C-C cases.

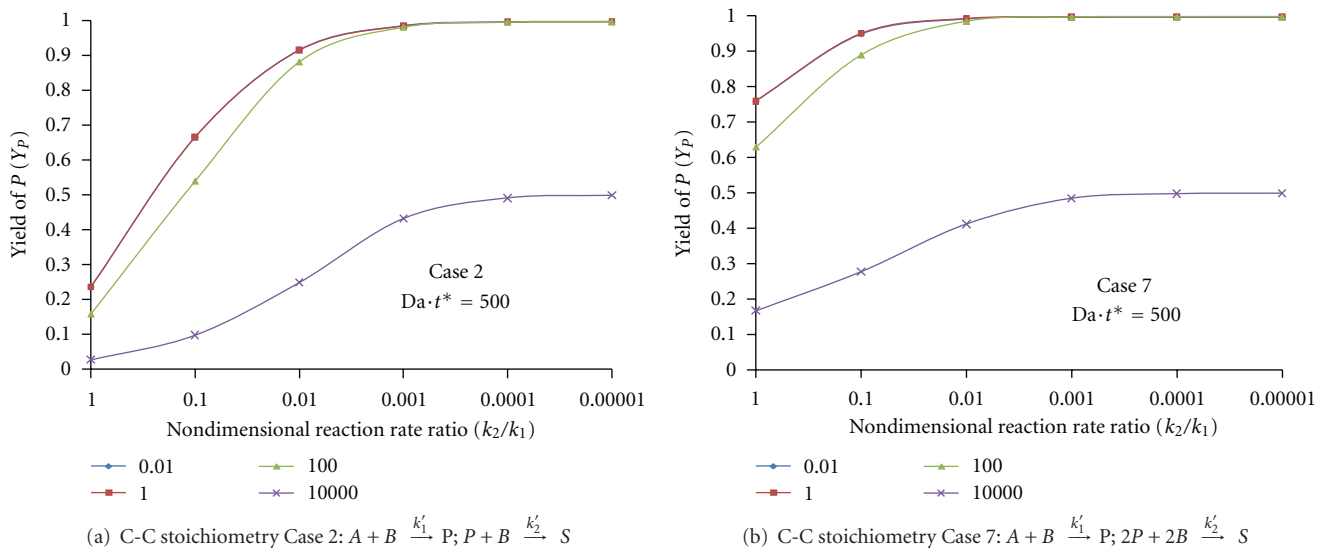


FIGURE 3: Plots of Yield of P versus k_2/k_1 for two sample C-C stoichiometries. The curves represent the different Da . Curves for $Da = 0.01$ lie exactly under the curves for $Da = 1$.

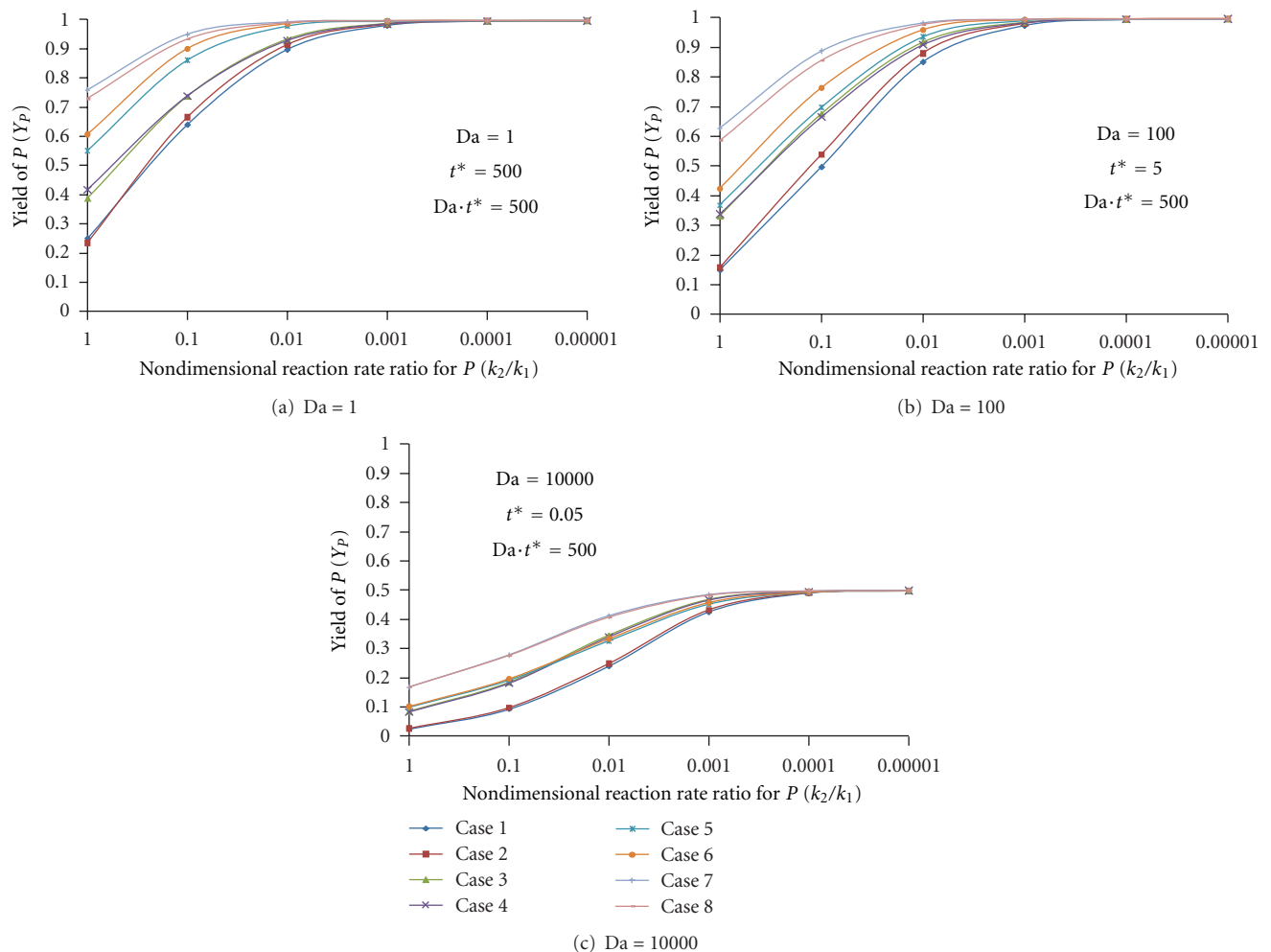


FIGURE 4: Plots of yield of P versus k_2/k_1 for various Da at $Da \cdot t^* = 500$ for C-C cases.

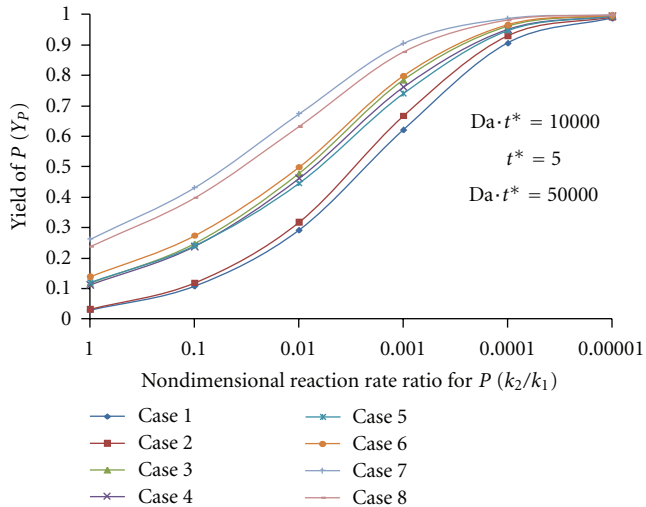


FIGURE 5: Plot of yield of P versus k_2/k_1 for $Da = 10000$ at $Da \cdot t^* = 50000$ for C-C cases.

The base data is presented in Figure 6, with selected data replotted in Figures 79.

3.2.1. Effect of Damköhler Number (Da). The plots in Figure 6 show a large drop in Y_P when Damköhler number increases from 100 to 10000 with the exception of Case 3 at $k_2/k_1 = 1$ where the yield increases steadily with increasing Da . Case 3 is the only stoichiometry where the desired reaction consumes more molecules than the undesired reaction, so when the reaction rates are equal and mixing is good, the mass transfer limitation on the desired reaction will push the yield toward the secondary reaction. Since the reactions are parallel, there is no barrier to the production of S over P .

For the C-P reaction pair, yield is constant for $Da \leq 100$, giving a well-mixed limit of $Da = 100$. Figures 7(a) and 7(b) confirm this result for Cases 1 and 3, respectively. The curves show the four values of Da investigated. The curves for $Da = 0.01$ and $Da = 1$ lie exactly on top of each other and the curve for $Da = 100$ is very close, but increasing Da to 10 000 drops the yield significantly. These results are very similar to the C-C results. It is concluded that $Da = 100$ is the well-mixed limit for C-P reactions.

3.2.2. Effect of Dimensionless Reaction Rate Ratio (k_2/k_1). Looking at Figure 6 from the perspective of reaction rate ratio, as k_2/k_1 is decreased, the curves for all the stoichiometries move upwards, increasing the yield for all cases at all values of Da . As expected, a smaller k_2/k_1 increases the yield of desired product. For Cases 1 and 2 the maximum yield is approximately 1 and for Cases 3 and 4 it is 0.88. The curves for Cases 1 and 2 collapse at $k_2/k_1 = 0.001$ (Figure 6(d)) and the curves for Cases 3 and 4 collapse at $k_2/k_1 = 0.0001$ (Figure 6(e)). The largest change with improving k_2/k_1 is seen for Case 3, while Case 2 improves the least. These trends are confirmed in Figure 8, showing a persistent effect of stoichiometry on the maximum attainable yield. The poorly mixed condition ($Da = 10\ 000$) may not have reached

completion at $Da \cdot t^* = 500$ since the yield is only about 50%.

In Figure 9 the poorly mixed condition is allowed to progress 100x longer. At this point, the yield can increase to above 90% but only for a 100x smaller k_2/k_1 ratio. The curves seem to collapse at $k_2/k_1 = 0.00001$, but at lower k_2/k_1 's the effect of stoichiometry persists, even at long times. Once again, 100x more residence time and 100x better chemistry are required to eliminate all the effects of 100x worse mixing.

3.2.3. Effect of Stoichiometry. Figures 6(a) to 6(f) illustrate a significant effect of stoichiometry for the C-P case. At $k_2/k_1 = 1$ (Figure 6(a)) the difference in yield for the different stoichiometries is enormous, and there is a clear distinction between the most favourable and least favourable reaction stoichiometries (Case 2 and Case 3, respectively). This difference decreases as k_2/k_1 decreases (Figures 6(b) to 6(f)). For the C-P scheme, the effect of stoichiometry persists even at $k_2/k_1 = 0.00001$, where the difference in yield between Cases 1 and 2 and Cases 3 and 4 is more than 10%. This is different from the C-C stoichiometries where the effect of stoichiometry disappeared by $k_2/k_1 \leq 0.001$.

Referring to Table 3, Cases 1 and 4 require the same number of molecules for both reactions, while Case 2 favors the desired reaction (fewer molecules) and Case 3 favors the side reaction. Case 3 is the only case of all 12 stoichiometries considered where the desired reaction consumes more molecules than the side reaction, imposing a mass transfer and collision probability limitation on the desired reaction. This explains the dramatically different results observed for Case 3 and suggests that this class of reaction stoichiometry must be handled more carefully than the others.

3.2.4. Summary of Results for the C-P Reaction Scheme. For competitive-parallel reactions, we have the following.

- $Da \leq 100$ is the well-mixed limit for all k_2/k_1 .
- For all cases with favourable stoichiometries, at $Da \cdot t^* = 500$, $k_2/k_1 \leq 0.001$ provides the maximum yield, as for the C-C reaction scheme, but for the C-P reaction scheme the maximum yield depends on the stoichiometry. Case 3, the only case with an unfavourable stoichiometry, requires $k_2/k_1 \leq 0.0001$ to achieve maximum yield.
- Stoichiometry affects the maximum obtainable yield to some degree for all mixing conditions and all k_2/k_1 .
- As for the C-C scheme, increasing the number of molecules in the side reaction imposes a mass transfer limitation on that reaction, making conditions more favorable for the desired reaction. Case 3 in the C-P scheme clearly illustrates that when the desired reaction consumes more molecules than the undesired reaction, it is more difficult to achieve a high yield of desired product.

3.3. Phase Plots of Variables for C-C And C-P Reaction Schemes for the Purpose of Design. The purpose of design

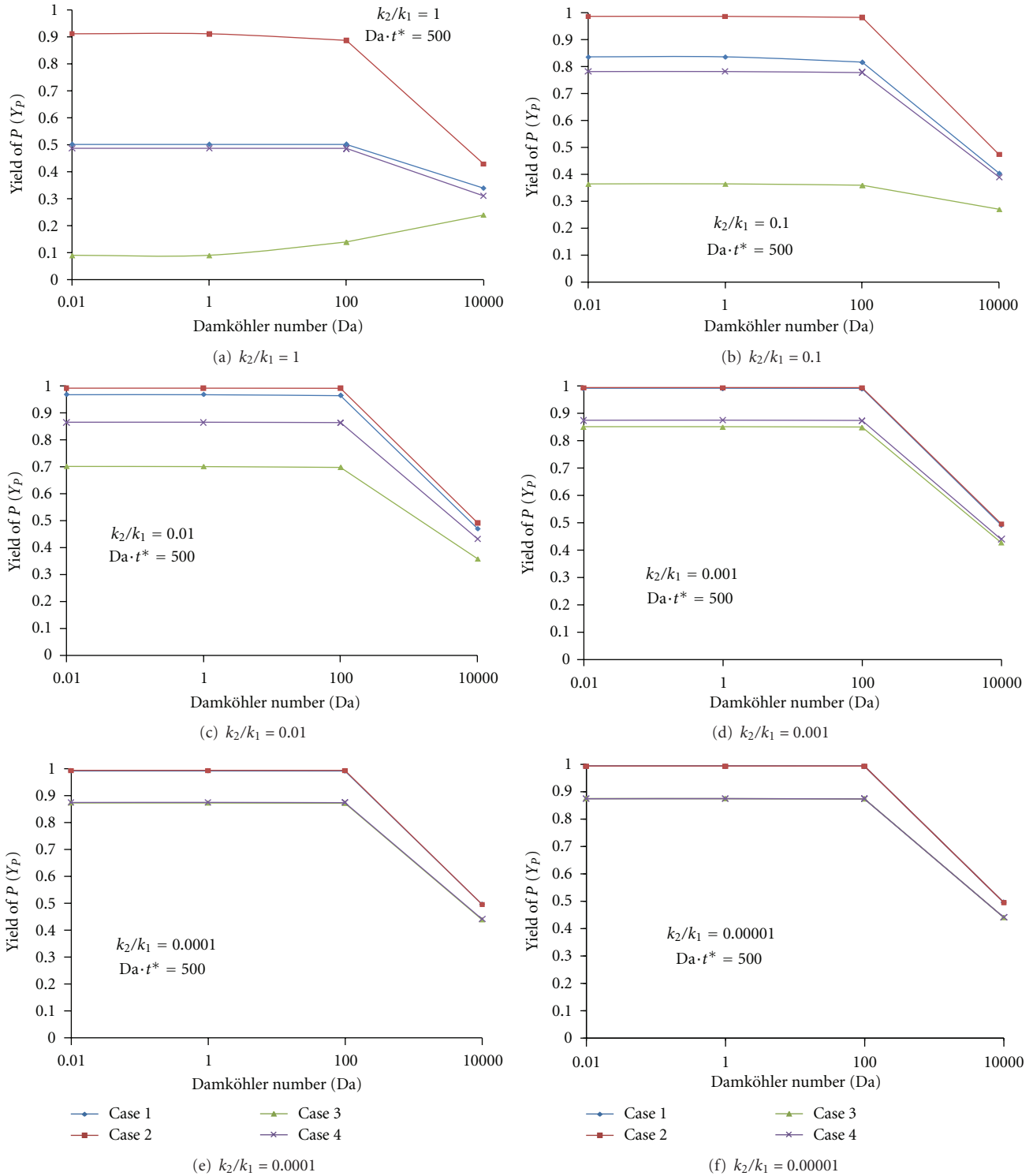


FIGURE 6: Plots of yield of P versus Da for decreasing k_2/k_1 ratios for the C-P cases.

graphs, in the context of mixing sensitive reactions, is to provide a direct method of predicting the yield of desired product without extensive calculations and investigation of the different variables. For our purposes, design graphs would incorporate the effects of stoichiometry, mixing, and k_2/k_1 and the combinations of the three that could possibly

give a certain specified yield of desired product. The purpose of the graphs would be to assist in the design of the following problem.

“If one has a certain mixing sensitive reaction and a target yield of desired product in mind, what

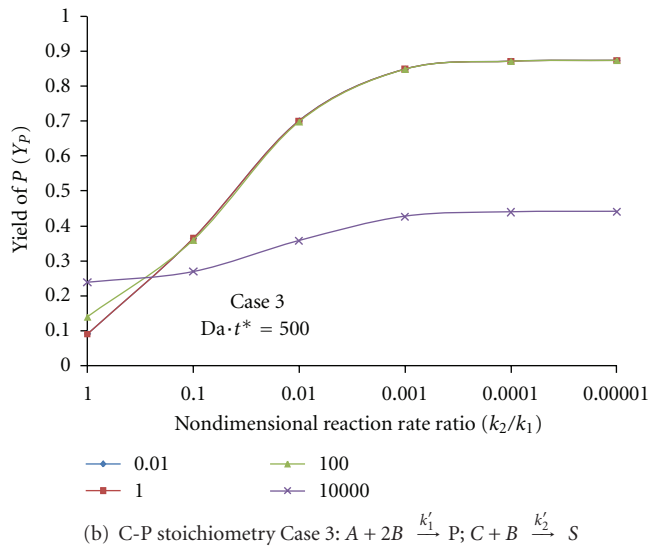
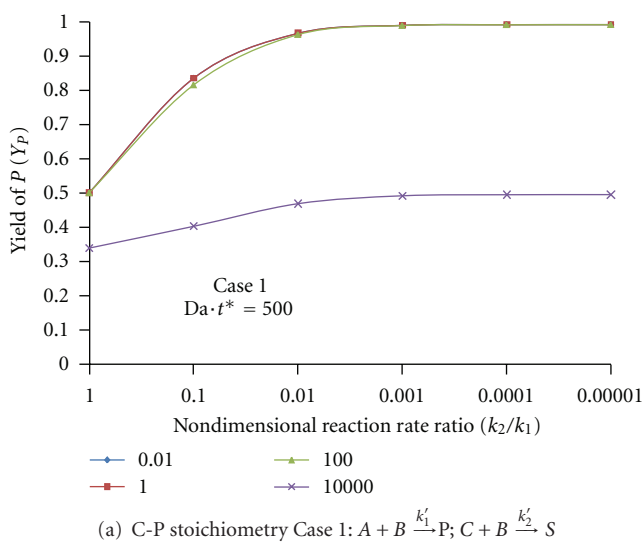


FIGURE 7: Plots of yield of P versus k_2/k_1 for two sample C-P stoichiometries. The curves represent the different Da. Curves for Da = 0.01 lie exactly under the curves for Da = 1.

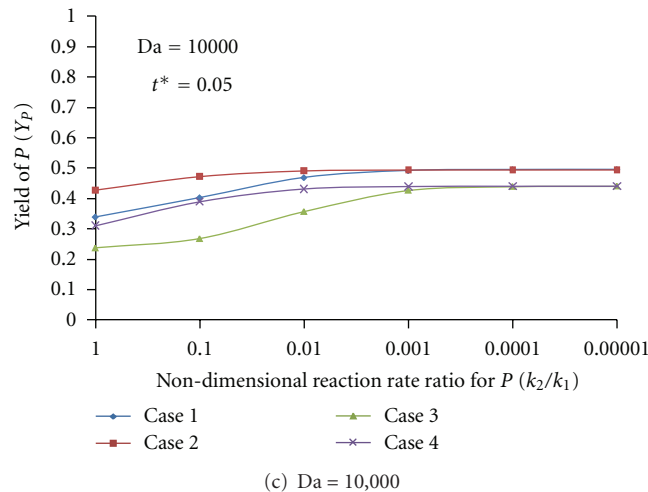
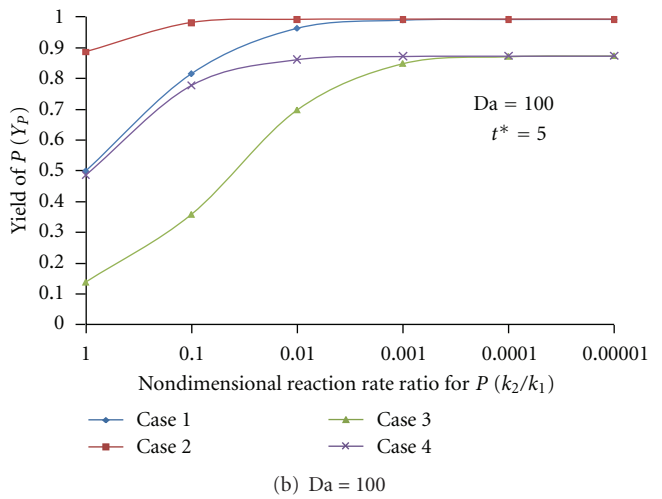
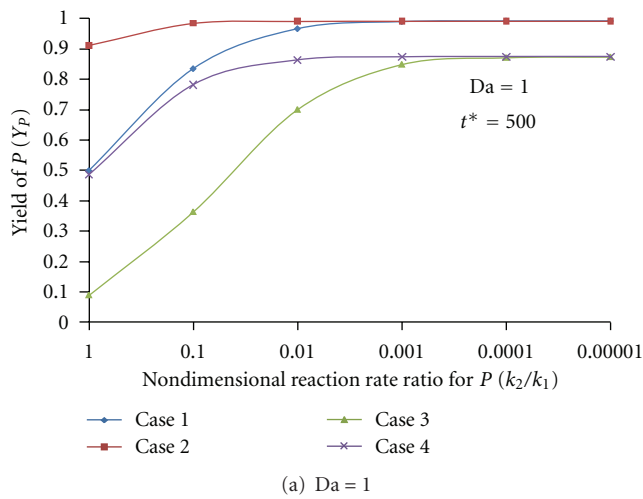


FIGURE 8: Plots of yield of P versus k_2/k_1 for various Da at Da · t* = 500 for C-P cases.

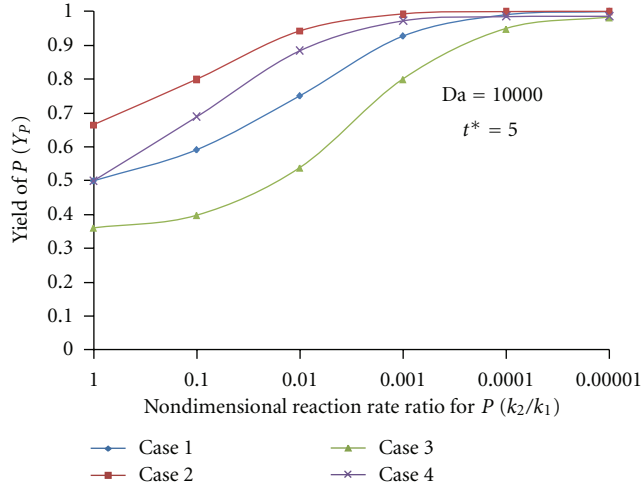


FIGURE 9: Plot of yield of P versus k_2/k_1 for $Da = 10000$ at $Da \cdot t^* = 50000$ for C-P cases.

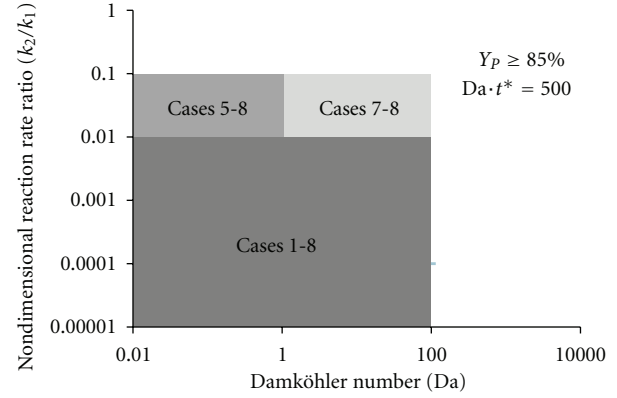
range of values of dimensionless reaction rate ratio and Damköhler would be required to ensure that the target yield of desired product will be obtained? If one of the variables is inadequate, is it still possible to obtain the target yield? If it is possible, how much do the other variables need to change to accommodate for that inadequacy, if at all?"

The figures should allow for a design space to be established within which decisions can be made based on different criteria and restrictions.

Figure 10 and Figure 11 show the required Damköhler number (x -axis) versus the dimensionless reaction rate ratio (y -axis) for yields of desired product of (a) 85% or more, (b) 95% or more, and (c) 99% or more at a time of $Da \cdot t^* = 500$. They are set up such that the axis intersection (origin) represents the most favourable conditions for both k_2/k_1 and Damköhler number. The figures have marked regions of required k_2/k_1 and Da where a specified yield can be obtained for different stoichiometries. These figures are essentially a filtered summary of the results presented in the previous sections. The effect of stoichiometry quickly becomes evident as the specified yield is increased. For the C-C cases, the requirements on the k_2/k_1 and Da become more stringent as Y_P increases. For C-P Cases 3 and 4, yields greater than 90% were unachievable for $Da \cdot t^* = 500$.

In order to link these results to physical process variables, the diffusion time is replaced with an analogous mixing time scale for turbulent flow. The Batchelor time scale gives the diffusion time for a Kolmogorov sized eddy and is numerically equal to the Kolmogorov time scale, which is the lifetime of the same smallest eddy before the momentum is diffused by viscosity. Replacing the molecular diffusion time in a slab in our definition of Da with the expression for the Kolmogorov time scale in a turbulent eddy gives the following:

$$Da = k'_1 \left(\frac{\rho_T}{M} \right)^\epsilon \left(\frac{\nu}{\epsilon_D} \right)^{1/2} \quad (5)$$



(a) Y_P is at least 0.85 (85%)

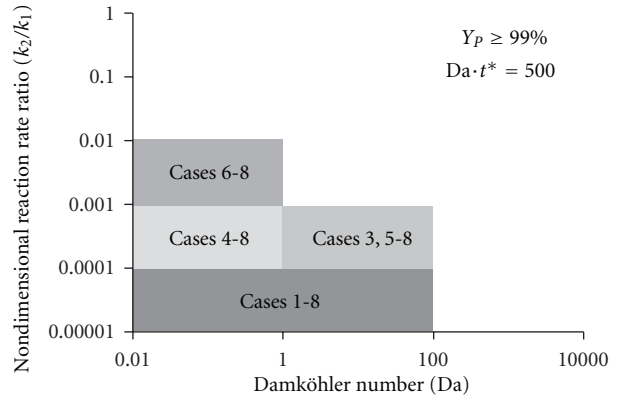
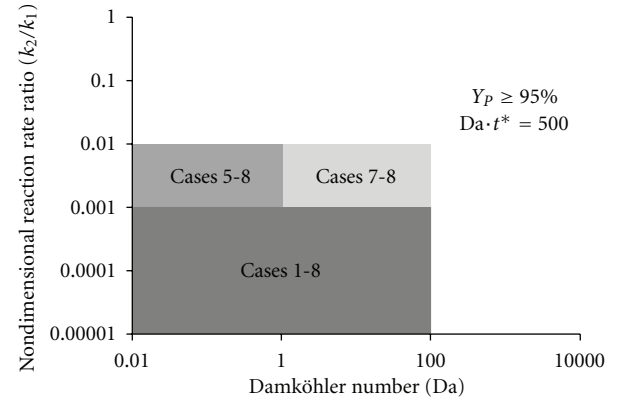


FIGURE 10: Design spaces for yield of P for Da and k_2/k_1 at $Da \cdot t^* = 500$ for C-C cases.

where ν is the kinematic viscosity and ϵ_D is local rate of dissipation of turbulent kinetic energy (TKE) per mass. Rearranging to solve for ϵ_D gives the following:

$$\epsilon_D = \nu \left(\frac{k'_1 (\rho_T/M)^\epsilon}{Da} \right)^2 \quad (6)$$

This expression proposes a relationship between the rate of dissipation of turbulent kinetic energy (ϵ_D), the reaction kinetics of the desired reaction (k'_1), and the reaction stoichiometry (ϵ) which might be used to compare bench scale performance with the Da and reaction rate ratio from the phase plot. For example, for a C-C reaction of the type

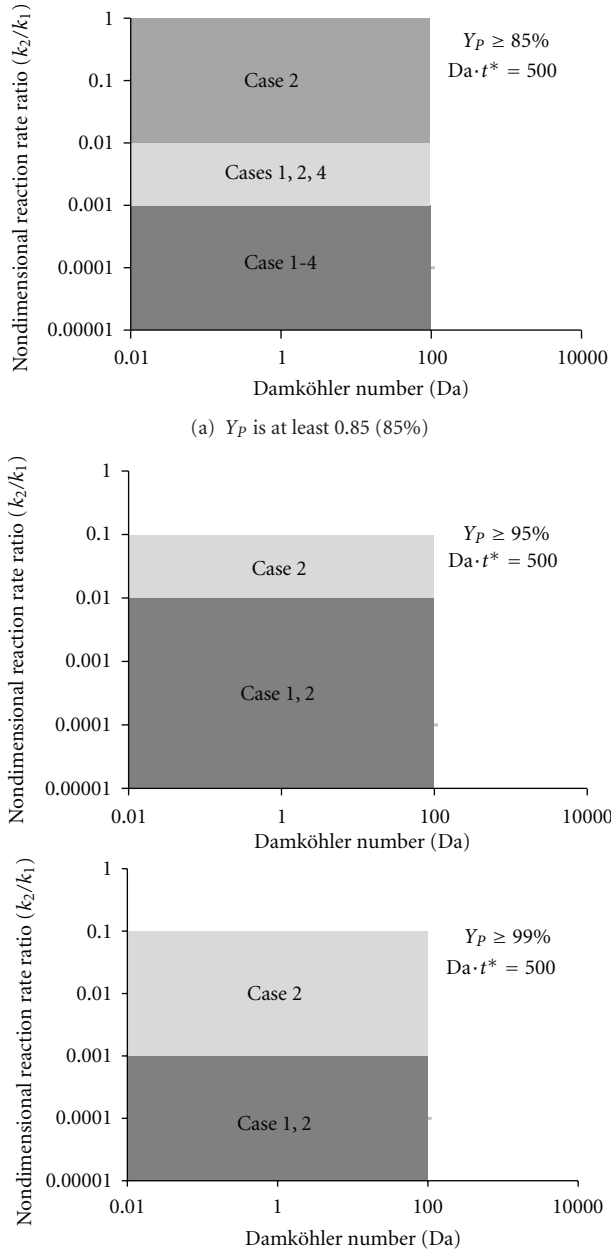


FIGURE 11: Design spaces for yield of P for Da and k_2/k_1 at $Da \cdot t^* = 500$ for C-P cases.

Case 1 ($\epsilon = 1$), using typical values for water ($\nu = 1 \times 10^{-6}$ m²/s, $\rho_T = 1000$ kg/m³, $M = 18$ kg/kmole), ϵ_D for $Da = 1$ becomes

$$\epsilon_D = 3.09 \times 10^{-3} k_1'^2. \quad (7)$$

This gives a first-order estimate for the required level of dissipation at the bench scale. Since the model is based on a static striation thickness rather than the dynamic stretching and cutting field present in both chaotic and turbulent flows, this should be considered a starting point for further investigations in the context of more accurate models of mixing and diffusion.

4. Conclusions

The three effects of initial mixing condition, dimensionless reaction rate ratio, and reaction stoichiometry were investigated in detail using a 1D, transient, reaction-diffusion model for competitive-consecutive (C-C) and competitive-parallel (C-P) reactions. It was found that smaller values of Damköhler number and dimensionless reaction rate ratio are desirable to maximize the yield of desired product for both the C-C and C-P reaction schemes. It was also found that the stoichiometry of the reaction can affect the final yield of desired product considerably and needs to be taken into consideration in the design of reactors for such reactions. The following limits were found for each of the variables.

- (i) $Da \leq 1$ is the well-mixed limit for the C-C reaction when $k_2/k_1 \geq 0.01$. With $k_2/k_1 \leq 0.01$, the well-mixed limit can be relaxed to $Da \leq 100$.
- (ii) $Da \leq 100$ is the well-mixed limit for all k_2/k_1 for the C-P reaction.
- (iii) $k_2/k_1 \leq 0.001$ with $Da \leq 100$ provides the maximum yield at $Da \cdot t^* = 500$ for both the C-C and the C-P reactions with favourable stoichiometries. For the C-P case with the most unfavourable stoichiometry $k_2/k_1 \leq 0.0001$ is required.
- (iv) The effect of stoichiometry is significant. Where the secondary reaction consumes more molecules than the primary reaction, it is subject to a mass transfer constraint which favors the primary reaction. For the C-P scheme the effect of stoichiometry is persistent, affecting the final yield by more than 10% even for a well-mixed case with favorable k_2/k_1 .

The model used here is intended to illustrate the importance of the previously uninvestigated effect of stoichiometry on the yield of desired product and to provide general forms of the Damköhler number and reaction rate ratio for C-C and C-P reactions. The results are not intended to give accurate predictions of yield but to illustrate the trends in a quantitative way. It is hoped that the results will guide development of experimental reaction schemes which serve as mixing probes and development of more realistic reactor models which incorporate mixing, reaction kinetics, and stoichiometry.

Nomenclature

- Da : Damköhler number [-]
 D : Diffusivity [m²/s]
 k_1' : Rate constant 1 [m³/kmols]
 k_2' : Rate constant 2 [varies]
 $\frac{k_2}{k_1}$: Dimensionless reaction rate ratio [-]
 L : Striation thickness [m]
 M : Molecular weight [kg/kmol]
 R : Reaction term [kg/m³ s]
 t : Time [s]

t^* : Dimensionless time [–]
 w : Mass fraction [–]
 x : Distance [m]
 x^* : Dimensionless distance [–]
 Y_p : Yield of desired product P [–].

Greek Letters

$\alpha, \beta, \gamma, \epsilon$: Stoichiometric coefficients [–]
 ϵ_D : Local dissipation of turbulent kinetic energy per mass [m^2/s^3]
 ρ : Mass concentration [kg/m^3]
 ν : Kinematic viscosity [m^2/s]
 τ_M : Mixing time [s]
 τ_R : Reaction time [s].

Subscripts

A: Species A (reactant)
 B: Species B (reactant)
 C: Species C (reactant)
 i: Species A, B, C, I, P, or S
 I: Species I (inert)
 0: Initial value
 P: Species P (product)
 S: Species S (byproduct)
 T: Total
 Y, Z: Species mixtures.

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