

EFFECT OF STOICHIOMETRY ON YIELD FOR COMPETITIVE CONSECUTIVE MIXING SENSITIVE REACTIONS

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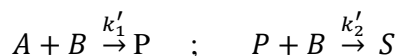
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Abstract. When a reaction is nearly instantaneous it is often mixing limited, i.e. the progress of the reaction depends on how fast the reactants are brought together. The effect of mixing is especially evident in the case of a Competitive-Consecutive reaction scheme where the product of the desirable reaction reacts further to form undesirable by-products. Recent experimental results suggest that the mixing effect may depend strongly on the reaction stoichiometry. A 1-D, non-dimensionalized, diffusion-reaction model at the micromixing scale has been developed to characterize this reactive-diffusive system. Constant density and diffusivities were assumed and the system of PDE's was solved using COMSOL 3.4. It was found that the ratio of rate constants, the stoichiometry and the striation thickness can all have considerable effects on the yield. A general Damkohler number and dimensionless reaction rate ratio were derived for the case of varying stoichiometry.

Key words: homogeneous reaction, mixing, Damkohler number, reaction-diffusion equation, micromixing

1. INTRODUCTION

All chemical reactions require intimate mixing of reagents and contact at the molecular scale. Some reactions are slow, so the reagents are completely mixed, or homogeneous, before the reaction takes place. These reactions tend not to be mixing sensitive. However, there are also reactions which are very fast or near instantaneous, where the reaction takes place as soon as the reagents are brought together. Since the rate of reaction is often much faster than the rate of mixing, these instantaneous reactions tend to be highly sensitive to mixing, thereby leading to large gradients in the local concentrations of reactants and products. This is especially true in the case of a competitive-consecutive (C-C) reaction where the product of the first reaction reacts with one of the original reagents to form a byproduct, as represented by the classic C-C reaction scheme:



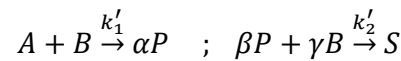
For a perfectly homogeneous mixture of reactants, with $k_1' \gg k_2'$ and the stoichiometric ratio of the two reactants equal to one (A:B = 1:1), the yield of byproduct should be very small. Previous investigations [1, 2, 3]; however, have shown that the yield of byproduct can be quite significant. This is due to poor mixing. The aim of this study is to develop a reaction-diffusion model at the micromixing scale to investigate the effects of mixing, the relative reaction rates of the first reaction and second reactions, and the previously undocumented

effect of stoichiometry on the yield of desired product. This is similar to the work of Cox et al [4,5,6], who investigated the effects of mixing and of relative rates of reaction for only the classical C-C reaction scheme given above. The extensive related literature on the reaction diffusion problem applied to the case of various chaotic flows is not addressed here.

2. MODEL DESCRIPTION AND NUMERICAL DETAILS

2.1 Theory

A system of non-dimensional reactive-diffusive Partial Differential Equations (PDE's) based on a mass balance has been developed for a single phase, stationary, isothermal system of alternating reactants A and B with constant cross-sectional area, as shown in Figure 1. The effect of stoichiometry is captured by the generalisation of the C-C reaction scheme represented by:



where A and B are the initial reactants, P is the desired product and S is the undesired by-product. k'_1 and k'_2 represent the rate constants for the first and second reactions respectively and α, β, γ are the stoichiometric coefficients varied to obtain different reaction schemes. This allows for the exploration of mass transfer limitations associated with more complex underlying reaction mechanisms, some of which might be modelled as a C-C reaction. Constant and equal densities (ρ_T) and diffusivities (D_B) are assumed for all four species in the system. Reactants A and B are always assumed to be present in an initial ratio of 1:1 and their molecular weights (M_A, M_B) are assumed to be equal (M). Molecular weights of P and S depend on stoichiometry and are derived from the equations. The initial striations of A and B are of equal thickness (L_B) and constant cross-sectional area, allowing the use of 1-D equations. A mass balance is preferred over the more traditional mole balance since mass is conserved for all stoichiometries, whereas moles are not always conserved. The equations can be converted from mass to mole basis as necessary.

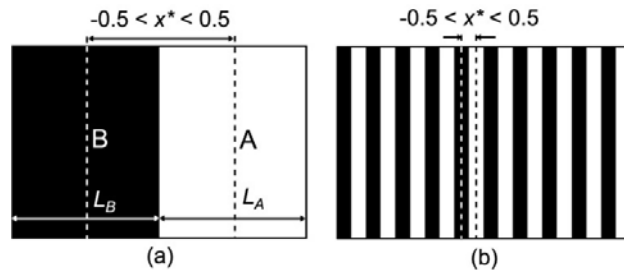


Figure 1. System geometry

Using the following non-dimensionalizing variables for space (x) and time (t):

$$x^* = \frac{x}{L_B} \quad (1); \quad t^* = \frac{t D_B}{L_B^2} \quad (2)$$

and converting species densities (ρ_i) to mass fractions (w_i) using the following relations:

$$\rho_T = \sum \rho_i \quad (3); \quad w_i = \frac{\rho_i}{\rho_T} \quad (4); \quad \sum w_i = 1 \quad (5)$$

the non-dimensional general species equations for this 1-D, stationary, reactive-diffusive system for a C-C reaction with a general stoichiometry can be written as:

$$\frac{\partial(w_i)}{\partial t^*} = \frac{\partial^2(w_i)}{\partial x^{*2}} + \frac{L_B^2}{\rho_T D_B} R_i \quad (6)$$

where R_i represents the source and sink terms for each species arising from the reactions. These terms were obtained by assuming both reactions to be elementary, and converting molar rate expressions to mass fraction rate expressions by multiplying the molar rate expression by the corresponding molecular weight of each species. For species A:

$$R_A \left[\frac{\text{mass}}{m^3 S} \right] = -k'_1 [A][B] M_A = -k'_1 \frac{\rho_A}{M_A} \frac{\rho_B}{M_B} M_A = -k'_1 \frac{\rho_T^2}{M} w_A w_B \quad (7)$$

The resulting full species mass balance equations with reaction terms replaced are:

$$\text{A: } \frac{\partial(w_A)}{\partial t^*} = \frac{\partial^2(w_A)}{\partial x^{*2}} - \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} w_A w_B \right) \quad (8)$$

$$\text{B: } \frac{\partial(w_B)}{\partial t^*} = \frac{\partial^2(w_B)}{\partial x^{*2}} - \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} w_A w_B \right) - \gamma \left(k'_2 \left(\frac{\rho_T}{M} \right)^{\beta+\gamma-1} \left(\frac{\alpha}{2} \right)^\beta \frac{L_B^2}{D_B} w_P^\beta w_B^\gamma \right) \quad (9)$$

$$\text{P: } \frac{\partial(w_P)}{\partial t^*} = \frac{\partial^2(w_P)}{\partial x^{*2}} + 2 \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} w_A w_B \right) - \frac{2\beta}{\alpha} \left(k'_2 \left(\frac{\rho_T}{M} \right)^{\beta+\gamma-1} \left(\frac{\alpha}{2} \right)^\beta \frac{L_B^2}{D_B} w_P^\beta w_B^\gamma \right) \quad (10)$$

$$\text{S: } \frac{\partial(w_S)}{\partial t^*} = \frac{\partial^2(w_S)}{\partial x^{*2}} + \left(\frac{2\beta}{\alpha} + \gamma \right) \left(k'_2 \left(\frac{\rho_T}{M} \right)^{\beta+\gamma-1} \left(\frac{\alpha}{2} \right)^\beta \frac{L_B^2}{D_B} w_P^\beta w_B^\gamma \right) \quad (11)$$

The $\frac{\alpha}{2}$ terms arise from the fact that M_P is not always equal to M . If we define a non-dimensional reaction rate ratio for species P derived from the rate expressions such that:

$$\frac{k_2}{k_1} = \frac{\text{mass rate of Consumption of P}}{\text{mass rate of Production of P}} = \left[\frac{\beta}{\alpha} \left(\frac{\alpha}{2} \right)^\beta \left(\frac{\rho_T}{M} \right)^{\beta+\gamma-2} \right] \left[\frac{k'_2}{k'_1} \right] = \frac{1}{C} \left[\frac{k'_2}{k'_1} \right] \quad (12)$$

Equations 8-11 can then be re-written as:

$$\text{A: } \frac{\partial(w_A)}{\partial t^*} = \frac{\partial^2(w_A)}{\partial x^{*2}} - \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} \right) w_A w_B \quad (13)$$

$$\text{B: } \frac{\partial(w_B)}{\partial t^*} = \frac{\partial^2(w_B)}{\partial x^{*2}} - \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} \right) w_A w_B - \left(\frac{\alpha\gamma}{\beta} \right) \left[\frac{k_2}{k_1} \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} \right) w_P^\beta w_B^\gamma \right] \quad (14)$$

$$\text{P: } \frac{\partial(w_P)}{\partial t^*} = \frac{\partial^2(w_P)}{\partial x^{*2}} + 2 \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} \right) w_A w_B - 2 \left[\frac{k_2}{k_1} \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} \right) w_P^\beta w_B^\gamma \right] \quad (15)$$

$$\text{S: } \frac{\partial(w_S)}{\partial t^*} = \frac{\partial^2(w_S)}{\partial x^{*2}} + \left(2 + \frac{\alpha\gamma}{\beta} \right) \left[\frac{k_2}{k_1} \left(k'_1 \frac{\rho_T}{M} \frac{L_B^2}{D_B} \right) w_P^\beta w_B^\gamma \right] \quad (16)$$

This physically meaningful $\frac{k_2}{k_1}$ captures the effect of stoichiometry as well as the effect of ratio of the reaction rate constants. As a result, a stoichiometry independent Damkohler number falls out of the general equations:

$$Da = k_1' \frac{\rho_T L_B^2}{M D_B} \quad (17)$$

This Da depends on the rate constant of the first reaction and the initial striation thickness, so it scales the rate of diffusion at the smallest scale of mixing with the most rapid reaction rate in the system.

2.2 COMSOL solver

COMSOL Multiphysics 3.4, a commercial Finite Element solver, was used to solve the system of four non-dimensional equations highlighted above, of which only three are independent. The 1-D, transient, convection and diffusion mass transport model was used, with the mass fractions for each species specified as the independent variables. The default Lagrange-quadratic element was chosen. A 1-D geometry line of unit length and equally split into two sub-domains was specified and a mesh of 2048 equally spaced elements was generated. The following Boundary Conditions (BC's) were specified:

$$\frac{\partial w_A}{\partial x^*} = \frac{\partial w_B}{\partial x^*} = \frac{\partial w_P}{\partial x^*} = \frac{\partial w_S}{\partial x^*} = 0 \text{ at } x^* = -1/2 \text{ and } x^* = 1/2 \text{ for all } t^* \quad (18)$$

and the following Initial Conditions (IC's) were specified:

$$w_A(t^* = 0) = 1 \text{ for } -1/2 \leq x^* < 0 \quad (19)$$

$$w_B(t^* = 0) = 1 \text{ for } 0 \leq x^* \leq 1/2 \quad (20)$$

2.3 Design of Simulations

The main objective of this study was to examine the effect of stoichiometry on mixing sensitive competitive-consecutive reactions. The values of α, β, γ were set to either 1 or 2 giving 8 distinct stoichiometries, as shown in Table 1. The non-dimensional $\frac{k_2}{k_1}$ for each stoichiometry is given in terms of the actual rate constant ratio, $\frac{k_2'}{k_1'}$. To more clearly demonstrate the effect of stoichiometry on the non-dimensional reaction rate ratio, values of C for Equation 12 are given for the case of water ($\rho_T = 1 \frac{kg}{L}$, $M = 18 \frac{kg}{kmol}$). The ratio $\frac{k_2}{k_1}$ was varied between 1 and 10^{-5} in multiples of 10, giving a total of six levels, with a smaller number indicating a more favorable ratio. Da was set to 0.01, 1, and 100.

In total there were 144 converged simulations. All the simulations were run either until steady state values of mass fractions for all species were obtained, i.e. all of the B was consumed, or the equivalent of $t^* = 500$ for $Da=1$ was reached, whichever came first. Since the simulations were run in non-dimensional time, the times taken to reach completion were scaled by Damkohler number. The relationship between the non-dimensional times for each of the Damkohler numbers is given by:

$$t_{Da=0.01}^* = 100t_{Da=1}^* = 10000t_{Da=100}^* \quad (21)$$

Simulations for $Da=0.01$ were run to $t^*=50000$, for $Da=1$ to $t^*=500$, and for $Da=100$ to $t^*=5$.

Table 1. Reaction schemes investigated with values of the stoichiometry dependant terms.

Case	Reaction Scheme	α, β, γ	$\frac{\alpha\gamma}{\beta}$	$\frac{k_2}{k_1}$	C (for water, Eq 12)
1	$A + B \xrightarrow{k_1'} 2P$ $P + B \xrightarrow{k_2'} S$	2, 1, 1	2	$\frac{1}{2} \frac{k_2'}{k_1'}$	2
2	$A + B \xrightarrow{k_1'} P$ $P + B \xrightarrow{k_2'} S$	1, 1, 1	1	$\frac{1}{2} \frac{k_2'}{k_1'}$	2
3	$A + B \xrightarrow{k_1'} P$ $2P + B \xrightarrow{k_2'} S$	1, 2, 1	$\frac{1}{2}$	$\frac{1}{2} \left(\frac{\rho_T}{M}\right) \frac{k_2'}{k_1'}$	36
4	$A + B \xrightarrow{k_1'} 2P$ $2P + B \xrightarrow{k_2'} S$	2, 2, 1	1	$\left(\frac{\rho_T}{M}\right) \frac{k_2'}{k_1'}$	18
5	$A + B \xrightarrow{k_1'} 2P$ $P + 2B \xrightarrow{k_2'} S$	2, 1, 2	4	$\frac{1}{2} \left(\frac{\rho_T}{M}\right) \frac{k_2'}{k_1'}$	36
6	$A + B \xrightarrow{k_1'} P$ $P + 2B \xrightarrow{k_2'} S$	1, 1, 2	2	$\frac{1}{2} \left(\frac{\rho_T}{M}\right) \frac{k_2'}{k_1'}$	36
7	$A + B \xrightarrow{k_1'} P$ $2P + 2B \xrightarrow{k_2'} S$	1, 2, 2	1	$\frac{1}{2} \left(\frac{\rho_T}{M}\right)^2 \frac{k_2'}{k_1'}$	648
8	$A + B \xrightarrow{k_1'} 2P$ $2P + 2B \xrightarrow{k_2'} S$	2, 2, 2	2	$\left(\frac{\rho_T}{M}\right)^2 \frac{k_2'}{k_1'}$	324

3.0 RESULTS AND DISCUSSION

COMSOL returns the profiles of mass fraction for the four species over the non-dimensional space x^* for each time step t^* . These profiles were integrated for each time step to get the variation of mass per unit area of each species with time. In order to get a yield for product P (Y_P), the integrated mass was divided by a maximum theoretical yield of P. Since A and B are present in equal amounts initially, this maximum yield of P is always 100% of the total mass. Therefore, a simple integration of mass fraction of P over space for each time step gives us the yield of P (Y_P).

$$Y_P(t^*) = \frac{\text{mass of species P at } t^*}{\text{maximum mass of P obtainable}} = \frac{\int_{-0.5}^{0.5} w_P dx^*(t^*)}{1} = \int_{-0.5}^{0.5} w_P dx^*(t^*) \quad (22)$$

The yield of P was plotted over time for the eight stoichiometries for varying Da and $\frac{k_2}{k_1}$. A sample set of these results is shown in Figure 2. The final Y_P 's for $Da=0.01$ and $Da=1$ are plotted versus $\frac{k_2}{k_1}$ as shown in Figure 3.

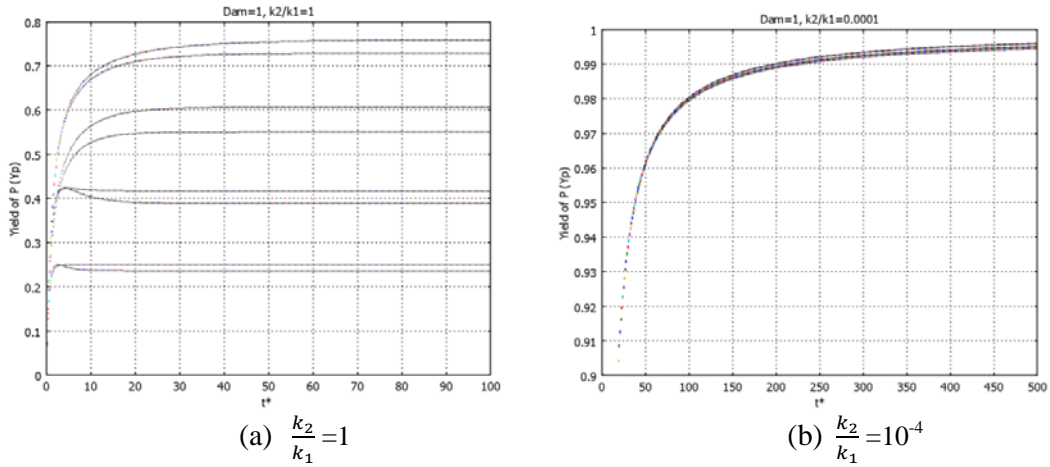


Figure 2. Plots showing the evolution of Y_P over non-dimensional time for $Da=1$.

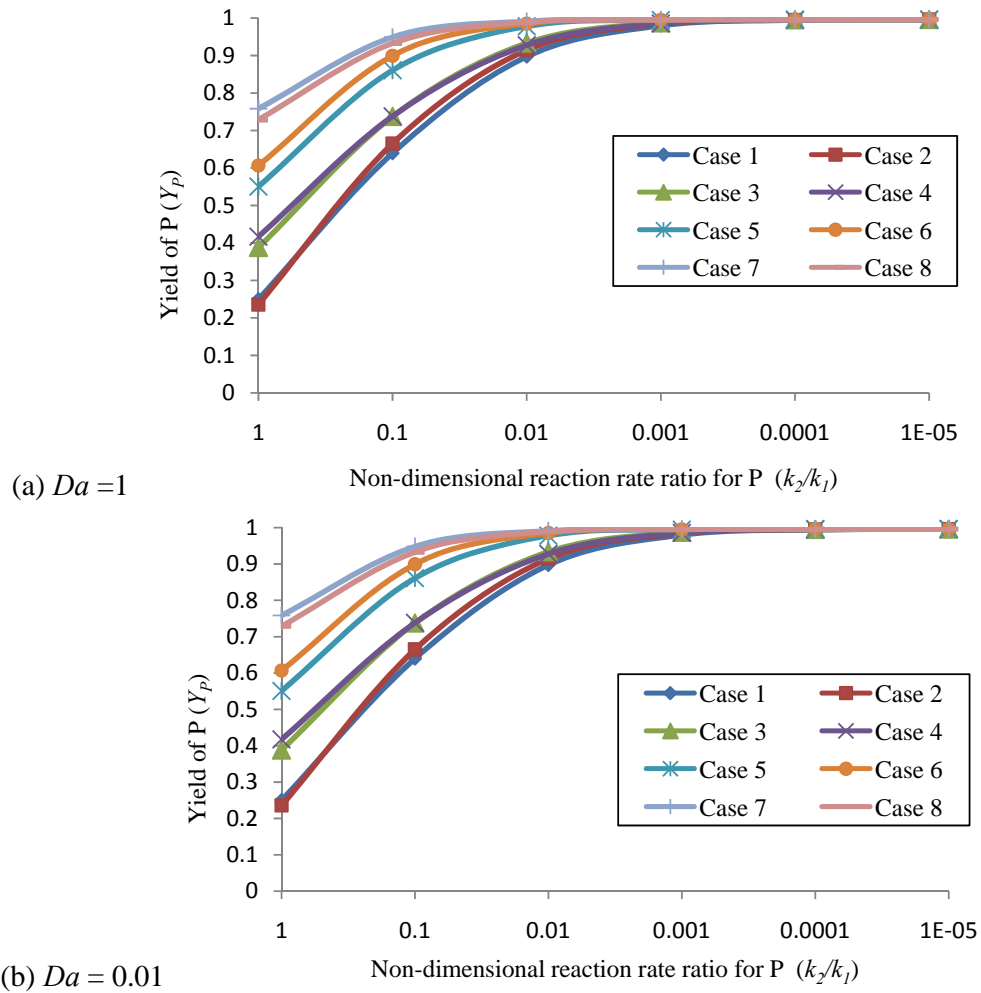


Figure 3. Final Y_P for the eight stoichiometry cases as $\frac{k_2}{k_1}$ decreases at (a) $Da=1$ and (b) $Da=0.01$. The horizontal axis is a log scale. The figures are identical, indicating that $Da=1$ is the threshold for perfect mixing.

3.1 Effect of stoichiometry

There is a large effect of stoichiometry on Y_P at high values of $\frac{k_2}{k_1}$ (left hand side of Figures 2(a) and 3), with some stoichiometries giving yields three times smaller than others. The effect of stoichiometry on the yield disappears at very low values of $\frac{k_2}{k_1}$, (right hand side of Figures 2(b) and 3). In order to keep a constant $\frac{k_2}{k_1}$ the actual reaction rate ratio $\frac{k_2'}{k_1}$ must increase to accommodate changes in the stoichiometry, as illustrated in the last column of Table 1. Returning to Figure 3, Cases 1 and 2 are the most sensitive to $\frac{k_2}{k_1}$, and Case 7 is the most robust. The stoichiometry of cases 3-6 requires more molecules for the second reaction, so these results confirm that mass transfer will limit the second reaction more than the first reaction for the higher order cases.

3.2 Well mixed limit ($Da \leq 1$)

As Figures 3(a) and (b) show, there is negligible change in Y_P for all eight stoichiometry cases when Da is reduced from 1.0 to 0.01, over the full 10^5 range of $\frac{k_2}{k_1}$. It is concluded that the well mixed limit is at $Da=1$ since there is no further change in product distribution when the striation thickness is reduced by 10 times to give $Da=0.01$. A $Da=1$ means that the diffusion time for the reactants is equal to the initial reaction rate for the first reaction, so this is also reasonable from a physical standpoint. Simulations for $Da>1$ show complex effects of mixing, but are not reported here due to lack of space.

3.3 Effect of non-dimensional reaction rate ratio $\left(\frac{k_2}{k_1}\right)$

Figure 3 shows that decreasing the $\frac{k_2}{k_1}$ ratio increases the yield of P for all eight stoichiometry cases at the well mixed limit. Both Figures 2 and 3 show that at a higher $\frac{k_2}{k_1}$ there are large differences in the yield of P for the different stoichiometry cases but these differences in Y_P diminish as $\frac{k_2}{k_1}$ is reduced until the yield of P for all eight stoichiometries converges to the same profile, as shown in Figure 2(b). Figure 3 clearly shows complete convergence at $\frac{k_2}{k_1} \leq 10^{-4}$ with only very small variation at $\frac{k_2}{k_1} \leq 10^{-3}$. What this means is that if the mass rate of consumption of P is a thousand times slower than the mass rate of production of P for any stoichiometry, the same yield of product will be obtained. This result is only valid for the well mixed limit. Referring back to Table 1, cases 7 and 8 will require a ratio of raw rate constants 324 and 162 times larger than case 1 to achieve the same k_2/k_1 . The more realistic cases 3-6 require raw rate constants 9 or 18 times larger than for the classic reaction scheme.

4.0 CONCLUSIONS

A reactive-diffusive model for competitive-consecutive reactions based on a species mass balance was used to explore the effects of reaction stoichiometry, relative reaction rates and degree of mixing on the yield of desired product. A non-dimensional reaction rate ratio which includes the effects of stoichiometry, $\frac{k_2}{k_1}$, and a Damkohler number which is independent of the stoichiometry of the system have been obtained. The well mixed limit is found at $Da=1$. For large $\frac{k_2}{k_1}$ the yield is reduced and there is a sizeable effect of stoichiometry on the maximum

yield. A $\frac{k_2}{k_1}$ less than 10^{-3} is sufficient to obtain a consistent yield of product. The raw rate constant ratio, $\frac{k_2'}{k_1'}$, can differ by orders of magnitude with varying stoichiometry when $\frac{k_2}{k_1}$ is held constant.

5.0 NOMENCLATURE

C	Constant in Equation 12 , [vary]	t	Time, [s]
Da	Damkohler Number, [-]	t^*	Non-dimensional time, [-]
D_B	Diffusivity, [m ² /s]	w	Mass fraction, [-]
k_1'	Rate constant 1, [m ³ /kmol s]	x	Distance, [m]
k_2'	Rate constant 2, [varies]	x^*	Non-dimensional distance, [-]
$\frac{k_2}{k_1}$	Non-dimensional reaction rate ratio, [-]	Y_P	Yield of Product P, [-]
L_B	Striation thickness, [m]		
M	Molecular weight, [kg/kmol]		
R	Reaction term [kg/m ³ s]		

Subscripts

A	Species A (reactant)
B	Species B (reactant)
i	Species A, B, P or S
P	Species P (product)
S	Species S (by-product)
T	Total

Greek Letters

α, β, γ	Stoichiometric Coefficients, [-]
ρ	Density, [kg/m ³]

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