

EFFECTIVENESS FACTOR AND SELECTIVITY ESTIMATION FOR A PARALLEL REACTION SYSTEM

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Abstract—The case of double parallel reaction scheme taking place in a porous catalytic pellet is analyzed. Effectiveness factor expressions for both reactions are derived after matching asymptotic solutions strictly valid for small and large values of the Thiele moduli.

It is assumed that the kinetics of both reactions follow a general irreversible power law model, that isothermal conditions prevail and that external mass transfer, resistances are negligible.

Approximate results in terms of effectiveness factors compare fairly well with exact results obtained by numerical integration of the differential equations. Maximum deviation is below 10% and in most circumstances is around 3%.

INTRODUCTION

Many reactor design calculations involve the problem of a parallel reaction system in heterogeneous catalyst pellets. In such cases product distribution can be influenced by mass diffusion within the pellets and the effectiveness factor calculations can become an important and time consuming step (see Wheeler[1]).

For this reason there is a strong need for accurate and simple calculation methods for effectiveness factors in coupled reaction systems. In this line Wedel and Luss[2] and Gottifredi *et al.*[3, 4] developed rational expressions for the effectiveness factor based on matching techniques from the knowledge of asymptotic solutions. However these approximate solutions are only valid for the case of a single reaction.

Pawlowski[5] and Roberts[6] performed an asymptotic analysis for the case of parallel reactions assuming different values of reaction orders. Roberts[6] also developed expressions to estimate selectivity and the maximum effect of pore diffusion. More recently Cukierman and Lemcoff[7] developed approximate asymptotic expressions for the effectiveness factors when the Thiele moduli of both reactions are very large. They however considered much more complex kinetic expressions than in previous works.

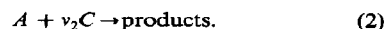
As far as the authors can ascertain, there is no analytic or approximate procedure to estimate the effectiveness factors of both reactions, except using numerical methods, for the whole range of Thiele moduli.

The aim of the present contribution is to show that a previously developed procedure to estimate effectiveness factor for complex reactions can also be used for the case of a double parallel independent reaction system. Isothermal conditions and uniform catalytic activity in a slab porous pellet will be

considered. However these are not strong limitations in solving the overall general problem as discussed previously[4].

ANALYSIS

Let us consider the following reaction scheme taking place in a porous slab catalyst pellet:



Assuming a power law kinetic expression for both reactions the dimensionless mass balance for species *A*, *B* and *C* can be written as:

$$\frac{d^2 C_A}{dX^2} = h_1^2 C_A^p C_B^m + h_2^2 C_A^q C_C^n \quad (3)$$

$$\frac{d^2 C_B}{dX^2} = \gamma_B h_1^2 C_A^p C_B^m \quad (4)$$

$$\frac{d^2 C_C}{dX^2} = \gamma_C h_2^2 C_A^q C_C^n \quad (5)$$

where *m*, *n*, *p* and *q* represent reaction orders and

$$h_1^2 = (k_1 C_{B_s}^m C_{A_s}^{p-1}) L^2 / D_A; \quad h_2^2 = (k_2 C_{C_s}^n C_{A_s}^{q-1}) L^2 / D_A$$

$$\gamma_B = \left(\frac{D_A C'_{AS}}{D_B C'_{BS}} \right) \nu_1; \quad \gamma_C = \left(\frac{D_A C'_{AS}}{D_C C'_{CS}} \right) \nu_2 \quad (6a-d)$$

C' being the dimensional concentration, *D* the effective diffusivity, *k*₁ and *k*₂ the specific kinetic reaction constants for reactions (1) and (2) respectively, *L* the half thickness of the slab pellet and subindexes *A*, *B*, *C* and *S* denote properties of species *A*, *B*, *C* and values evaluated at the external surface of the pellet respectively.

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The system (3)–(5) must be solved subject to the following boundary conditions

$$\begin{aligned} X=0 \quad C_A = C_B = C_C = 1 \\ X=1 \quad \frac{dC_A}{dX} = \frac{dC_B}{dX} = \frac{dC_C}{dX} = 0 \end{aligned} \quad (7a, b)$$

from which the following relation is easily found:

$$C_A - \frac{1}{\gamma_B} C_B - \frac{1}{\gamma_C} C_C = 1 - \left(\frac{1}{\gamma_B} + \frac{1}{\gamma_C} \right) = R \quad (8)$$

It will be assumed that $R > 0$ meaning that the concentration of special A under no circumstances can vanish. Since p , q , m and n are arbitrary the reaction system is so chosen that

$$r = \frac{h_2}{h_1} < 1. \quad (9)$$

The general solution of the system (3)–(5) is very difficult even with numerical methods. However it is possible to obtain asymptotic solutions when $h_1 \rightarrow 0$ and when $h_1 \rightarrow \infty$. In fact Cukierman and Lemcoff[7] have already presented the case where $h_1 \rightarrow \infty$ although it has not been compared with results generated by the numerical integration of the governing differential equations (3)–(5).

If $h_1 \rightarrow 0$ clearly $h_2 \rightarrow 0$ and following the perturbation procedure of Gottifredi *et al.*[3] up to terms to the order of h_1^2 or h_2^2 a series solution can be proposed:

$$C_B = 1 + h_1^2 B_1 + 0(h_1^4) \quad (10)$$

$$C_C = 1 + r^2 h_1^2 C_1 + 0(h_1^4) \quad (11)$$

and from eqn (8)

$$C_A = 1 + \left(\frac{h_1^2}{\gamma_B} \right) B_1 + r^2 \left(\frac{h_1^2}{\gamma_C} \right) C_1. \quad (12)$$

By replacing (10)–(12) in (4) and (5) and equating terms of like powers of h_1 , it can be shown that the following equations must be satisfied:

$$\frac{d^2 B_1}{dX^2} = \gamma_B \quad (13)$$

$$\frac{d^2 C_1}{dX^2} = \gamma_C \quad (14)$$

subject to:

$$x=0 \quad B_1 = C_1 = 0 \quad (15)$$

$$x=1 \quad dB_1/dx = dC_1/dx = 0. \quad (16)$$

After very simple algebraic steps it is possible to

show that under these assumptions:

$$\eta_1 = \int_0^1 C_A^p C_B^m dX = 1 - \sigma_1 h_1^2 + 0(h_1^4) \quad (17)$$

and

$$\eta_2 = \int_0^1 C_A^q C_C^n dX = 1 - \sigma_2 h_1^2 + 0(h_1^4) \quad (18)$$

where

$$\sigma_1 = \frac{1}{3} ((m\gamma_B + p) + pr^2) \quad (19)$$

$$\sigma_2 = \frac{1}{3} ((n\gamma_C + q)r^2 + q) \quad (20)$$

On the other hand when $h_1^2 \rightarrow \infty$ and $h_2^2 \rightarrow \infty$, Cukierman and Lemcoff[7] have shown that:

$$\eta_1 = \frac{\delta}{h_1} \quad (21)$$

$$\eta_2 = \frac{\rho}{rh_1} \quad (22)$$

where the parameter δ and ρ depend upon the values of m , n , p , q , r , γ_B and γ_C through the following expressions:

$$\begin{aligned} \delta = \left[\frac{2}{\gamma_B} \int_0^1 \left\{ 1 + \frac{1}{\gamma_B} (C_B - 1) + \frac{1}{\gamma_C} (C_B^w - 1) \right\}^p \right. \\ \left. \times C_B^m dC_B \right]^{1/2} \end{aligned} \quad (23)$$

$$\begin{aligned} \rho = \left[\frac{2}{\gamma_C} \int_0^1 \left\{ 1 + \frac{1}{\gamma_C} (C_C - 1) \right. \right. \\ \left. \left. + \frac{1}{\gamma_B} (C_C^{1/w} - 1) \right\}^q C_C^n dC_C \right]^{1/2}. \end{aligned} \quad (24)$$

These integrals must be evaluated through some suitable numerical technique. However, in an attempt to render the whole procedure analytical and taking into account that the reactions are taking place in the outer shell of the pellet and that eqns (23) and (24) can only be solved when p and q are both equal to "one" the terms in brackets in the integrals can be expanded assuming that $(C_B - 1) \ll 1$ and $(C_C - 1) \ll 1$. With this assumption we found:

$$\begin{aligned} \delta = \left(\frac{2}{\gamma_B} \right)^{1/2} \left\{ \frac{1}{(m+1)} - \frac{p}{(m+2)(m+1)} \right. \\ \left. \times \left(\frac{1}{\gamma_B} + \frac{w}{\gamma_C} \right) \right\}^{1/2} \end{aligned} \quad (25)$$

$$\begin{aligned} \rho = \left(\frac{2}{\gamma_C} \right)^{1/2} \left\{ \frac{1}{(n+1)} - \frac{q}{(n+2)(n+1)} \right. \\ \left. \times \left(\frac{1}{\gamma_C} + \frac{1}{w\gamma_B} \right) \right\}^{1/2} \end{aligned} \quad (26)$$

with

$$w = \left(\frac{\gamma_C}{\gamma_B} \right)^{1/2} r. \quad (27)$$

Some sample calculations have shown that eqns (25) and (26) predict fairly well values of δ and ρ . Maximum deviations are below 2% with r ranging between 0.2 and 0.8.

It could be argued that the condition $h_1 \rightarrow \infty$ does not necessarily imply $h_2 \rightarrow \infty$ but from a practical point of view that should be the situation because if $h_1 \rightarrow \infty$ and h_2 is small it means that the system of reaction will almost be uncoupled and so of small practical interest.

The procedure now follows the same fashion as in previous contributions (3) and (4). It will be assumed that η_1 and η_2 can be well represented in the whole range of h_1 values by the following expressions:

$$\eta_1 = a_1 \frac{(b_1 + h_1^2)^{1/2}}{(c_1 + h_1^2)} \quad (28)$$

and

$$\eta_2 = a_2 \frac{(b_2 + h_1^2)^{1/2}}{(c_2 + h_1^2)}. \quad (29)$$

After expanding eqns (28) and (29) for small and large values of h_1 and comparing the resulting expressions with eqns (17), (18), (21) and (22) we found that a_1 , a_2 , b_1 , b_2 , c_1 and c_2 are given by:

$$a_1 = \delta; \quad b_1 = (c_1/a_1)^2; \quad a_2 = (\rho/r); \quad b_2 = (c_2/a_2)^2 \quad (30a-d)$$

$$c_1 = \left(\frac{1}{2\sigma_1} \right) (1 \pm \sqrt{1 - 2\sigma_1 a_1^2}) \quad (31)$$

$$c_2 = \left(\frac{1}{2\sigma_2} \right) (1 \pm \sqrt{1 - 2\sigma_2 a_2^2}). \quad (32)$$

In those cases where the argument of the square root becomes negative this term is neglected as discussed by Gottifredi *et al.*[4]. Although some precision is lost the method is still straightforward and simple and the deviation between approximate and exact results of effectiveness factor is still acceptable for reactor design calculation purposes.

RESULTS AND DISCUSSION

Values of η_1 , and η_2 obtained with eqns (28) and (29) for different values of m , n , p , q , r , γ_C and γ_B were compared with their corresponding values generated by the numerical solution of the system (3)–(5). Exact values of η_1 and η_2 will be denoted by η_{1N} and η_{2N} respectively. They were calculated by the orthogonal collocation method outlined by Villadsen and Michelsen[8]. A change of variable $u = (1 - X^2)$ was made in the differential equations (4) and (5) and boundary conditions (7a, b) and the collocation

points were zeros of $P^{(1, -1/2)}(u)$. Up to five interior points, depending on h_1 values, were used and the effectiveness factors were evaluated by a quadrature formula.

In Tables 1–3 the effectiveness factor values obtained from the analytic expressions (columns headed by η_1 and η_2) and from the numerical method (η_{1N} and η_{2N}) are presented. It can be clearly seen that there is a very good agreement between approximate and exact values for the range of parameters investigated. Maximum deviation for η_1 and η_2 predictions are below 5 and 10% respectively which is fairly acceptable for most reactor engineering calculation purposes.

It should be noticed that theoretical results of Cukierman and Lemcoff[7] produce extremely good asymptotic values of effectiveness factor for large values of Thiele modulus. This was not investigated. Moreover the analytical prediction of their finding through expressions (23) and (24) is suitable for large values of h_1 as can be seen in Tables 1–3.

It can be concluded that the procedure presented may be safely used for estimating effectiveness factors when a parallel reaction scheme is considered. Moreover with this analytical procedure it is possible to take into account external mass transfer resistances as shown before[4].

CONCLUSIONS

This is the first attempt, as far as the authors can ascertain, to predict with an analytical approximate procedure the effectiveness factors of a set of parallel independent reactions taking place within a porous catalytic slab pellet. It was assumed that both reactions are well represented by an irreversible power law kinetic expression.

As shown in Tables 1–3 there is in general a fairly good agreement between corresponding η_1 and η_2 values predicted by our procedure and those obtained by a numerical technique. Maximum deviations for η_1 and η_2 predictions are below 5 and 10% respectively although a common figure for this deviation is about 3%. It should be stressed that with these very simple expressions it is possible to predict η_1 and η_2 values for the complete range of h_1 , and then h_2 values. Accordingly the selectivity is easily estimated as:

$$S_{1-2} = r^{-2}(\eta_1/\eta_2) \quad (33)$$

and the effect of mass transfer phenomena on it can be forecast along the reactor. In Fig. 1 the selectivity S_{1-2} is plotted as a function of h_1 for different cases. It can be seen that as the diffusional restriction becomes more severe the effect on the selectivity is increasingly important. In some cases this effect can be so notable that it can reverse the selectivity (see curve E).

With this simple procedure it is also possible to take into account the effect of external mass transfer resistances on the selectivity since the change of boundary conditions can be easily taken into account

Table 1.

h_1	m = 1						n = 1						p = 1						q = 1					
	$\chi_0 = 2; \chi = 2; r = 0.5$		$\chi_0 = 10; \chi = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$		$\chi_0 = 2; r = 0.5$	
	η_1	η_{1N}	η_2	η_{2N}	η_1	η_{1N}	η_2	η_{2N}	η_1	η_{1N}	η_2	η_{2N}	η_1	η_{1N}	η_2	η_{2N}	η_1	η_{1N}	η_2	η_{2N}	η_1	η_{1N}	η_2	η_{2N}
0.1	0.9893	0.9893	0.9950	0.9942	0.9642	0.9642	0.9964	0.9943	0.9881	0.9881	0.9904	0.9904	0.9630	0.9630	0.9630	0.9630	0.9630	0.9631	0.9631	0.9631	0.9630	0.9631	0.9915	0.9915
0.5	0.7997	0.8031	0.8944	0.8957	0.5624	0.5646	0.9195	0.9066	0.7834	0.7868	0.8185	0.8221	0.5558	0.5558	0.5558	0.5558	0.5558	0.5576	0.5576	0.5576	0.5558	0.5576	0.8355	0.8393
1	0.5425	0.5510	0.7071	0.7063	0.3052	0.3051	0.7601	0.7696	0.5235	0.5310	0.5771	0.5873	0.3010	0.3010	0.3010	0.3010	0.3010	0.3003	0.3003	0.3003	0.3010	0.3003	0.6053	0.6271
2	0.2986	0.3033	0.4472	0.4642	0.1530	0.1523	0.5049	0.5384	0.2875	0.2912	0.3311	0.3393	0.1510	0.1510	0.1510	0.1510	0.1510	0.1499	0.1499	0.1499	0.1510	0.1499	0.3554	0.3744
4	0.1523	0.1528	0.2425	0.2587	0.0763	0.0759	0.2807	0.3034	0.1469	0.1473	0.1723	0.1754	0.0754	0.0754	0.0754	0.0754	0.0754	0.0754	0.0749	0.0749	0.0754	0.0749	0.1867	0.1940
8	0.0764	0.0763	0.1240	0.1327	0.0381	0.0389	0.1447	0.1544	0.0738	0.0738	0.0870	0.0882	0.0377	0.0377	0.0377	0.0377	0.0377	0.0383	0.0383	0.0383	0.0377	0.0383	0.0946	0.0973

Table 2.

m = 2 ; n = 1 ; p = 1 ; q = 1								
$\gamma_B = 2 ; \gamma_C = 2 ; r = 0.5$					$\gamma_B = 2 ; \gamma_C = 2 ; r = 0.8$			
h_1	η_1	η_{1N}	η_2	η_{2N}	η_1	η_{1N}	η_2	η_{2N}
0.1	0.9829	0.9830	0.9950	0.9943	0.9817	0.9817	0.9904	0.9904
0.5	0.7270	0.7317	0.8944	0.8919	0.7159	0.7185	0.8185	0.8272
1	0.4646	0.4709	0.7071	0.7266	0.4545	0.4563	0.5771	0.6001
2	0.2524	0.2536	0.4472	0.4880	0.2466	0.2449	0.3311	0.3509
4	0.1291	0.1280	0.2425	0.2727	0.1261	0.1241	0.1723	0.1815
8	0.0649	0.0644	0.1240	0.1394	0.0634	0.0626	0.0870	0.0911

Table 3.

m = 1 ; n = 1 ; p = 2 ; q = 1					m = 2 ; n = 1 ; p = 1 ; q = 2			
$\gamma_B = 2 ; \gamma_C = 2 ; r = 0.5$					$\gamma_B = 10 ; \gamma_C = 2 ; r = 0.8$			
h_1	η_1	η_{1N}	η_2	η_{2N}	η_1	η_{1N}	η_2	η_{2N}
0.1	0.9853	0.9853	0.9950	0.9943	0.9344	0.9349	0.9869	0.9856
0.5	0.7454	0.7551	0.8944	0.8899	0.4526	0.4606	0.7747	0.7952
1	0.4714	0.4932	0.7071	0.7210	0.2431	0.2457	0.5224	0.5712
2	0.2485	0.2646	0.4472	0.4829	0.1238	0.1236	0.2929	0.3354
4	0.1249	0.1324	0.2425	0.2705	0.0622	0.0617	0.1514	0.1746
8	0.0625	0.0660	0.1240	0.1385	0.0311	0.0309	0.0764	0.0877

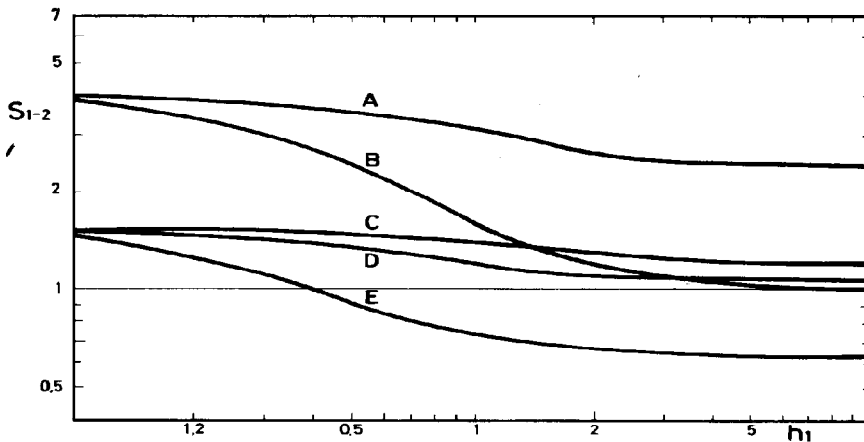


Fig. 1. Selectivity to reaction (1) S_{1-2} as a function of Thiele modulus h_1 . Curves A, B and C: $m = n = p = q = 1$ and $\gamma_B = \gamma_C = 2, r = 0.5$; $\gamma_B = 10, \gamma_C = 2, r = 0.5$; $\gamma_B = \gamma_C = 2, r = 0.8$ respectively. Curve D: $m = 2, m = p = q = 1, \gamma_B = \gamma_C = 2, r = 0.8$. Curve E: $m = 2, m = p = 1, q = 2, \gamma_B = 10, \gamma_C = 2, r = 0.8$.

with a trial and error procedure as previously shown[3].

The asymptotic solutions obtained for the case of $h_1^2 \rightarrow 0$ can also be used to generate criteria to establish the absence of mass transfer resistance inside the pellet.

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NOTATION

a_1, b_1, c_1	parameters defined by eqn (28)
a_2, b_2, c_2	parameters defined by eqn (29)
B_1	auxiliary expansion function defined by eqn (10)
C	dimensionless concentration
C_1	auxiliary expansion function defined by eqn (11)
D	effective diffusivity coefficient
h_1, h_2	Thiele modulus for reactions 1 and 2 respectively
k_1, k_2	reaction constants for reactions 1 and 2 respectively
L	half thickness of the slab
m	order of reaction for species B
n	order of reaction for species C
p, q	orders of reaction for species A in reaction 1 and 2 respectively

r	Thiele modulus ratio
R	constant defined by eqn (8)
x	dimensionless coordinate

Greek symbols

γ_B, γ_C	parameters defined by eqns (6c, d)
δ	parameter defined by eqn (21)
η_1, η_2	effectiveness factors for reaction 1 and 2
σ_1, σ_2	parameters defined by eqns (17, 18)
w	parameter defined by eqn (27)

Subindexes

A, B, C	for species A, B or C
S	surface value

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