Chemical Engineering Science 64 (2009) 2762 – 2766

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Shorter Communication

Evaluating the effectiveness factor from a 1D approximation fitted at high Thiele modulus: Spanning commercial pellet shapes with linear kinetics

Néstor J. Mariani[a,b], Clarisa Mocciaro[a,b], Sergio D. Keegan[a,b], Osvaldo M. Martínez[a,b], Guillermo F. Barreto[a,b,*]

[a]PROIRQ, Área Departamental Ingeniería Química, Facultad de Ingeniería, UNLP, La Plata, Argentina
[b]Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. J. J. Ronco" (CINDECA), CONICET-UNLP, Calle 47 No. 257, CC 59, CP B1900AJK, La Plata, Argentina

ARTICLE INFO

Article history:
Received 10 February 2009
Accepted 26 February 2009
Available online 9 March 2009

Keywords:
Chemical reactors
Catalysis
Porous media
Mass transfer
Effectiveness factor
One-dimensional model

ABSTRACT

In the present contribution a one-dimensional model (1D model) is employed to account for the effect of pellet shape in the solution of diffusion–catalytic reaction problems. The 1D model free parameter (σ) is fitted so as to match the second term of the series for the effective reaction rate at fast kinetic conditions. The performance of the model was evaluated for a large collection of pellets available commercially, covering almost all the main shapes offered by catalyst manufacturers. For isothermal linear kinetics the effectiveness factors calculated by the 1D model differ at most by 3% from those of the actual 3D pellets.

1. Introduction

The numerical solution of the conservation balances in two (2D) or three (3D) spatial coordinates for the diffusion-reaction problem in actual catalytic pellets is normally a time consuming operation, even for the simplest practical case (e.g. simulation of a catalytic reactor with a single reaction). For this reason, it becomes highly desirable to reduce the spatial dimension of the problem.

A flexible one-dimensional model (1D model) formerly proposed by Datta and Leung (1985) was adopted for this task. The adjustable parameter σ (shape factor) of this model—called here generalized cylinder (GC)—is fitted so as to match the second term of the series for the effective reaction rate at fast kinetic conditions in catalytic pellets (Mariani et al., 2008).

Employing the above stated criterion the performance of the 1D-GC model was evaluated for a large set of pellet shapes. Up to the best of our knowledge, such set covers essentially all pellet shapes considered in technical and scientific literature. Trilobes, poly-lobes, multi-holed particles, star-shaped rings, indented cylinders and geometries combining different features from the previous examples have been tested. In most cases the relative dimensions were taken from manufacturers' catalogs. Isothermal linear kinetics was employed for the comparison between the effective reaction rate from the actual 3D pellet and the 1D-GC model.

2. 1D model formulation

The 1D-GC model is introduced in order to replace the actual geometry of a given catalytic pellet by a simpler hypothetical body that allows mass and heat transport in only one spatial coordinate $0 < z' < L$ and presents a variable cross-section S^{GC} according to

$$S^{GC} = S_p(z'/L)^{\sigma} = S_p z^{\sigma},$$

where S_p is the permeable external area of the actual pellet. L (*diffusion length*) and σ (*shape factor*) are the model parameters.

The external surface in the model is at $z = 1$ and its area is the same as that of the actual pellet ($S^{GC} = S_p$, at $z = 1$). Nil mass and heat fluxes are assumed at $z = 0$. The volume V^{GC} of the model body,

$$V^{GC} = \int_0^L S_p\left(\frac{z'}{L}\right)^{\sigma} dz' = \frac{S_p L}{\sigma + 1}$$

is made equal to the actual pellet volume V_p. Hence, the diffusion length L becomes determined:

$$L = (\sigma + 1)l \tag{1}$$

where $l = V_p/S_p$ is the characteristic length of the actual pellet.

* Corresponding author at: PROIRQ, Área Departamental Ingeniería Química, Facultad de Ingeniería, UNLP, La Plata, Argentina.
E-mail address: barreto@quimica.unlp.edu.ar (G.F. Barreto).

0009-2509/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2009.02.044

For a single reaction and uniform activity ($a=1$), the conservation balance of a key species A (usually the limiting reactant) with uniform diffusion coefficient (D_A) is, according to the GC model:

$$z^{-\sigma}\frac{d}{dz}\left(z^{\sigma}\frac{dY}{dz}\right)=(1+\sigma)^2\Phi^2 r(Y) \tag{2a}$$

$$Y=1 \quad \text{at } z=1 \tag{2b}$$

$$dY/dz=0 \quad \text{at } z=0 \tag{2c}$$

where

$$Y=(C_A-C_{Ae})/(C_{As}-C_{Ae}) \tag{2d}$$

$$r=\pi_A/\pi_{As} \tag{2e}$$

where Y is a dimensionless concentration, C_A and π_A are the molar concentration and the net consumption rate of the A species, respectively; the subscript "s" denotes values at the pellet surface S_p and "e" refers to equilibrium conditions.

The Thiele modulus Φ is defined as

$$\Phi^2=l^2\frac{\pi_{As}}{D_A(C_{As}-C_{Ae})} \tag{3}$$

Values of σ are restrained by Eq. (1) to be greater than (-1). In addition, it is worth noting that the model exactly encompasses the classical 1D problems in a slab ($\sigma=0$), an infinitely long circular cylinder ($\sigma=1$) and a sphere ($\sigma=2$). The effectiveness factor is expressed as

$$\eta^{GC}=(1+\sigma)\int_0^1 r(Y)z^{\sigma}\,dz \tag{4}$$

Extending the procedure proposed by Wedel and Luss (1980) for a sphere to any value of σ, the effectiveness factor can be approximated for large values of Φ with the first two terms of a series in powers of $(1/\Phi)$:

$$\eta^{GC}_{high}=\frac{I_1}{\Phi}\left[1-\frac{I_{12}}{\Phi}\left(\frac{\sigma}{1+\sigma}\right)\right] \tag{5a}$$

where the coefficients I_1 and I_{12} depend on the specific reaction rate $r(Y)$ (see Keegan et al., 2005, 2006). For the isothermal first order reaction considered here, $r(Y)=Y$, $I_1=1$ and $I_{12}=1/2$.

Also, for $r(Y)=Y$, η^{GC} can be expressed by (Datta and Leung, 1985)

$$\eta^{GC}(\Phi)=\frac{1}{\Phi}\frac{I_{(\sigma+1)/2}[(1+\sigma)\Phi]}{I_{(\sigma-1)/2}[(1+\sigma)\Phi]} \tag{5b}$$

where I_t is the modified Bessel function of real order t. For non-linear kinetics, a numerical procedure or an approximation as that given by Keegan et al. (2003) should be employed to evaluate η^{GC}.

2.1. Criterion for adjusting σ

As can be appreciated in the truncated series (5a), the second order term contains the factor $\sigma/(1+\sigma)$ that just depends on the shape exponent σ. Provided that an expression similar to (5a) is available for the actual catalyst shape, the matching of the second order term will provide the value of σ. Keegan et al. (2005, 2006) developed a general formulation for the second order term, that can be expressed for the case of uniform catalytic activity as

$$\eta_{high}=\frac{I_1}{\Phi}\left[1-\frac{I_{12}}{\Phi}\Gamma\right] \tag{6}$$

The parameter Γ depends on the geometrical features of the actual pellet. Its external surface S_p can be decomposed into N_s smooth regions, i.e. pieces with continuous curvature, separated by N_w edges.

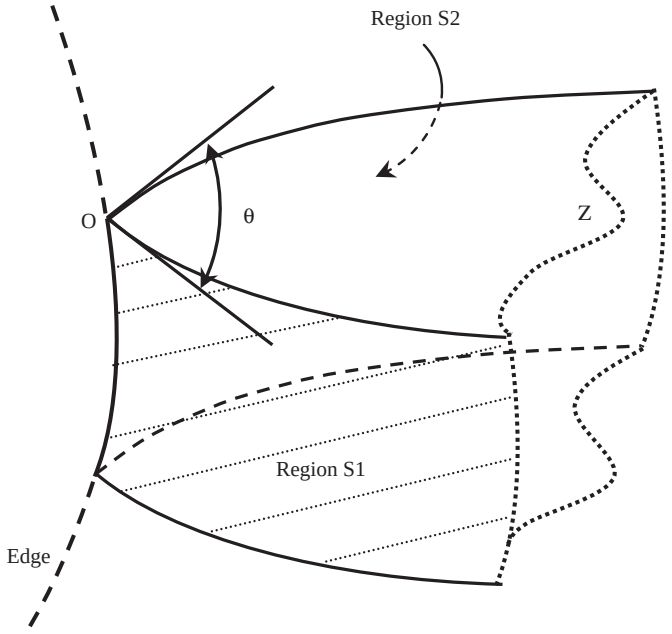


Fig. 1. Sketch showing the intersecting angle θ.

The smooth regions are geometrically characterized by the curvature parameter

$$\Psi=\frac{1}{R_a}+\frac{1}{R_b} \tag{7a}$$

where R_a and R_b are the local principal radii of curvature on the external pellet surface with the following sign convention: positive if the center of curvature is oriented towards the inside of the catalyst and negative in the opposite sense. If Ψ varies on a given smooth region v, the average on the area of the region S_v will account for the specific parameter Ψ_v of the region.

The edges are geometrically characterized by a parameter ω that strongly depends on the *intersecting angle* θ that a pair of smooth regions defines when they meet at the edge. The angle θ can be visualized in Fig. 1, where the pair of smooth regions are indicated by S1 and S2. For curved regions, θ will in general vary with the position on the edge. In Fig. 1, the plane Z normal to the edge at O allows identifying the local angle θ that corresponds to point O of the edge. The coefficient ω can be evaluated from the following approximation, which is strictly valid for first order reactions (Keegan et al., 2006):

$$\omega(\theta)=\begin{cases}\frac{8\ln 2}{\theta}\left[1-\left(\frac{\theta}{\pi}\right)^{\pi^2/(8\ln 2)}\right], & \text{si } 0\leqslant\theta\leqslant\pi\\ \frac{2\pi^2}{(\pi-2)\theta+\pi(4-\pi)}\left[1-\frac{\theta}{\pi}\right], & \text{si } \pi<\theta\leqslant 2\pi\end{cases} \tag{7b}$$

Although very weakly, $\omega(\theta)$ also depends on the specific kinetic expression $r(Y)$. A general expression for this purpose is given by Keegan et al. (2006).

For a given edge μ, averaging $\omega(\theta)$ along the edge length W_μ determines the specific parameter ω_μ of the edge. Now we are in position to write down the expression for Γ as developed by Keegan et al. (2006):

$$\Gamma=\frac{l}{S_p}\left[\sum_{v=1}^{N_s}\Psi_v S_v+\sum_{\mu=1}^{N_w}\omega_\mu W_\mu\right] \tag{8}$$

It is clear from Eqs. (5a) and (6) that the same asymptote $\eta\to I_1/\Phi$ will be obtained as $\Phi\to\infty$ (i.e. for the limiting regime) for both, the GC model and the actual pellet.

By matching the second terms in the series of Eqs. (5a) and (6), the parameter σ becomes

$$\sigma = \frac{\Gamma}{1-\Gamma} \tag{9}$$

Eq. (9) states the criterion proposed in this work to approximate the behavior of a given pellet by means of the 1D-GC model. By construction, the criterion guarantees that the GC model will be highly accurate at relatively large values of Φ. Also, differences will tend to zero if $\Phi \to 0$, as $\eta \to 1$ for both, the GC model and the actual pellet. The expectation, to be assessed in the next section, is that Eq. (9) imposed to the GC model will allow it to accurately approximate the actual values of η at intermediate values of Φ.

3. Results

A vast set of shapes corresponding mostly to commercially available catalysts has been considered to assess the performance of the 1D-GC model. The relative dimensions of pellets have been taken from manufacturers' catalogs (e.g. Haldor Topsoe, Criterion, Basf, Süd Chemie, Albermale, Johnson Matthey, Alvigo-Matros, UOP-Honeywell, UNICAT Catalyst Technologies). The catalysts whose shapes have been undertaken are intended for a variety of processes, like hydrogenations, isomerizations, oxidations, hydrotreatments, steam reforming, naphtha reforming, etc.

It should be pointed out that the analysis of shapes with high degree of symmetry (e.g. Raschig rings, tablets, etc.) has been undertaken previously with very good results: the GC model allows estimating the effective reaction rates with errors less than 2% for isothermal linear kinetics (Mariani et al., 2008).

The shapes and relative dimensions here analyzed are defined in Tables 1–3. Resulting values of the parameter σ (Eq. (9)) and the error ε_{max} (defined later on) are also included in those tables. The shapes in Tables 1 and 2 have been grouped by similarity and Table 3 includes miscellaneous shapes. All commercial pellets (all shapes except the hollow sphere and the torus in Table 3) are finite cylinders of different cross-section shapes.

As far as we know, the hollow sphere and the torus in Table 3 are not commercially available. They have been included in this study to extend the analysis to non-cylindrical shapes and, at the same time, they are potentially useful, because of being geometrically simple and offering similar advantages as the group in Table 2. In particular the torus can be also convenient for liquid or gas/liquid processes as the internal surface will be easily accessible under any position of the particle with respect to the direction of the main fluid-flow.

The effectiveness factor for the shapes in Tables 1–3 and $r(Y) = Y$ was evaluated with the software Femlab v3.1 of Comsol Inc that can solve the 3D conservation balance by the finite element method, while in the case of 1D-GC model Eq. (5b) was used.

Recalling that for each pellet geometry the parameter Γ (Eq. (8)) should be calculated in order to define the GC parameter σ (Eq. (9)), it is convenient to remark that for all shapes in Tables 1–3, but the torus in Table 3, the smooth regions in which S_p is decomposed show uniform curvature Ψ. For the cylinders, considering that the flat bases have no curvature, the only non-zero contributions Ψ_ν to Eq. (8) correspond to circular sectors of the cylindrical envelopes; hence, for any of them $\Psi_\nu = 1/R_\nu$, where R_ν is the circle radius (the other principal curvature radius is ∞). Besides, if φ_ν is the angle of the circular sector ν, $S_\nu = \varphi_\nu R_\nu H$, where H is the cylinder length. Hence the contribution of the circular sector ν in Eq. (8) is

$$S_\nu \Psi_\nu = \varphi_\nu H \tag{10a}$$

For the cylinders in Tables 1–3 there are close edges around the bases that show an intersection angle $\theta = \pi/2$ and co-axial edges also showing a constant θ; hence, the contribution of any wedge μ to Eq. (8) can be written

$$W_\mu w_\mu = W_\mu \omega(\theta_\mu) \tag{10b}$$

From Eqs. (8) and (10) it follows that

$$\text{(for finite cylinders)} \quad \Gamma = \frac{V_p}{S_p^2}\left[H\sum_{\nu=1}^{N_c}\varphi_\nu + \sum_{\mu=1}^{N_w} W_\mu \omega(\theta_\mu)\right] \tag{11}$$

where N_c is the number of circular sectors.

Note that the evaluation of the angles φ_ν and θ_μ can be conveniently done from the shape of the cross-section (Tables 1–3). As they already should be identified for calculating V_p and S_p and the use of Eq. (7b) to calculate ω is simple, it is concluded that for finite cylindrical pellets the evaluation of Γ—and hence of σ, Eq. (9)—is straightforward.

The parameter σ ranges from a slightly negative value $\sigma = -0.065$ (shape 10H in Table 2), i.e. less than for a slab ($\sigma = 0$) till values considerably higher than for sphere ($\sigma = 2$), as for the shapes 4L and 8L in Table 1: $\sigma = 3.08$ and 4.12, respectively.

The toroidal particle (Torus) in Table 3 shows a single smooth region for which the average of the curvature parameter Ψ (Eq. (7a)) is $\Psi_{torus} = 1/a$ (Buffham, 2000). Besides, $l = a/2$. It follows from Eqs. (8) and (9) that $\Gamma = 1/2$ and $\sigma = 1$ (the same values as for an infinitely long circular cylinder).

Table 1
Cross-section of multi-lobe particles; $y = a/b$ and $x = H/(H+b)$.

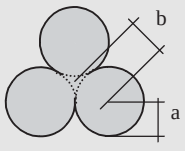
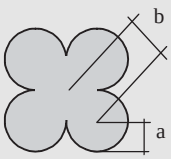
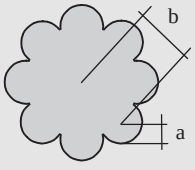
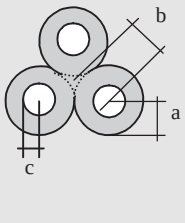
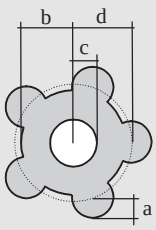
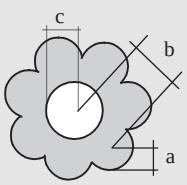
Particle	Trilobe (3L)	Quadralobe (4L)	8-lobes (8L)	Trilobe 3-holed ring (3L-3H)	Modified 5-lobes central holed ring (5ML-1H)	7-lobes central holed ring (7L-1H)
Cross-section						
Dimensions	$y = 0.866$ $x = 0.684$	$y = \frac{1}{\sqrt{2}}$ $x = 0.639$	$y = 0.383$ $x = 0.657$	$y = 0.866$ $c = 0.5a$ $x = 0.684$	$y = 0.394$ $c = 1.14a$ $d = 2.82a$ $x = 0.739$	$y = 0.434$ $c = 1.29a$ $x = 0.684$
l/b	0.355	0.321	0.295	0.203	0.231	0.222
σ	2.73	3.08	4.12	0.467	0.795	1.017
ε_{max}	0.75	0.47	1.46	1.27	0.56	0.53

Table 2
Cross-section of multi-holed particles; $y = a/b$ and $x = H/(H+b)$.

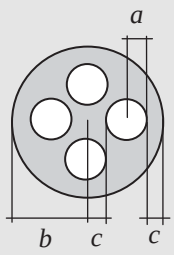
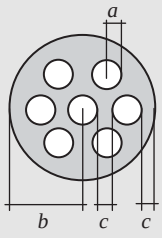
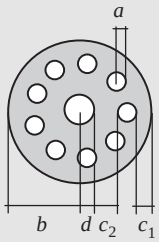
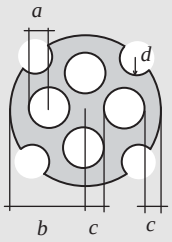
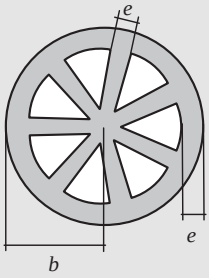
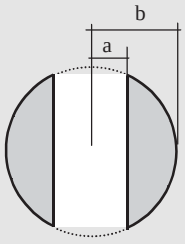
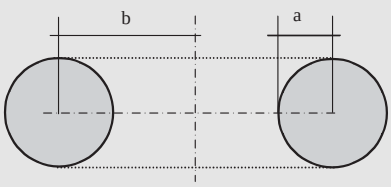
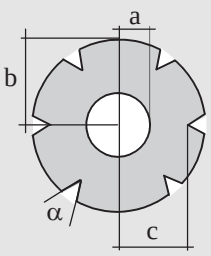
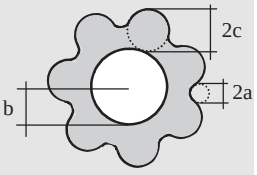
Particle	4-Holed ring (4H)	7-Holed ring (7H)	10-Holed ring (10H)	Modified 4-holed ring (4HM)	7-Holed spoke ring (7SR)
Cross-section					
Dimensions	$y = 0.273$ $c = 0.833a$ $x = 0.645$	$y = 1/5$ $c = a$ $x = 0.649$	$y = 1/8$ $c_1 = 1.6a$ $c_2 = 2.4a$ $d = 2a$ $x = 0.615$	$y = 1/4$ $c = a$ $d = 0.831a$ $x = 0.723$	$e = 0.2b$ $x = 0.477$
l/b	0.142	0.129	0.139	0.140	0.091
σ	0.195	0.029	−0.065	0.121	0.415
ε_{max}	2.88	2.12	2.93	1.26	0.54

Table 3
Miscellaneous particles; $y = a/b$ and $x = H/(H+b)$.

Particle	Holed sphere (HS)	Toroidal (T)	Star-shaped ring (SSR)	6-notches central holed ring (7L-1H)	Rounded star-shaped ring (RSSR)
Section					
Dimensions	$y = 0.5$	$y = 0.5$	$y = 0.292$ $x = 0.783$	$y = 0.367$ $c = 2.18a$ $\alpha = 1.047$ $x = 0.667$	$y = 2/9$ $c = 3a$ $x = 0.853$
l/b	0.167	0.250	0.354	0.207	0.425
σ	0.674	1.00	1.5	1.258	0.469
ε_{max}	1.16	0.10	2.80	0.94	0.20

For a given pellet shape the error of the GC model in estimating η is defined as

$$\varepsilon = \frac{|\eta_{GC} - \eta|}{\eta} 100$$

In general, ε presents a maximum for some intermediate value of Φ, as expected from the discussion at the end of the previous section. Therefore, the maximum seems to be representative to assess the behavior of the GC model:

$$\varepsilon_{max} = \max_{\Phi}\{\varepsilon\}$$

The overall and most significant comment about the results for ε_{max} reported in Tables 1–3 is the fact that ε_{max} remains below 3%.

4. Conclusions

With the aim of thoroughly testing the 1D-GC model performance 14 shapes were identified from around ten different catalyst manufactures and analyzed along with two others non-commercial shapes. The set of pellet shapes includes trilobes, poly-lobes, multi-holed particles, star-shaped rings, indented cylinders and shapes combining different features from the previous cases. In almost all cases the characteristic dimensions were taken from manufacturers' catalogs. The accuracy provided by the 1D-GC model was very good in all cases: the errors bounded by a level of 3% will be tolerable in most practical applications.

Up to the best of our knowledge, the fourteen shapes covers essentially all pellet shapes considered in technical and scientific literature. Thus, any potential user of 1D-GC model can readily recognize the pellet shape of his/her interest and keep confident of obtaining accurate results.

We expect to report further studies to validate the use of the GC model with parameter Γ for a broaden set of conditions. The performance of the GC model with examples of non-linear kinetics and some of the pellet shapes considered here has been reported recently (Mariani et al., 2009). For the normal kinetics tried (always $\eta < 1$) errors of the GC model do not differ much from those for linear kinetics. However, results still in progress for abnormal kinetics ($\eta > 1$ in some range of Φ) show that the errors start to grow when the region of steady state multiplicity is approached. This fact will impose limits in the use of the GC model.

As discussed by Keegan et al. (2005, 2006), the formulation for Γ presented here is expected to hold for multiple-reaction systems. The use of the GC model for multiple reactions is most significant, as numerical solutions for 3D pellets demand a huge amount of calculations and frequently will present convergence problems. We believe that a systematic study in this direction will be most valuable.

Acknowledgments

The authors wish to thank the financial support of the following Argentine institutions: ANPCyT- SECyT (PICT N# 14/38336) and UNLP (PID N# 11/I100). N. J. M., O. M. M. and G. F. B. are Research Members of the CONICET. Clarisa Mocciaro holds a fellowship from the CONICET.

References

Buffham, B.A., 2000. The size and compactness of particles of arbitrary shape: application to catalyst effectiveness factors. Chemical Engineering Science 55, 5803–5811.

Datta, R., Leung, S.W.K., 1985. Shape generalized isothermal effectiveness factor for first-order kinetics. Chemical Engineering Communications 39 (1), 155–173.

Keegan, S.D., Mariani, N.J., Bressa, S.P., Mazza, G.D., Barreto, G.F., 2003. Approximation of the effectiveness factor in catalytic pellets. Chemical Engineering Journal 94 (2), 107–112.

Keegan, S.D., Mariani, N.J., Martínez, O.M., Barreto, G.F., 2006. Behaviour of catalytic pellets at high reaction rates. The effect of the edges. Industrial and Engineering Chemistry Research 45, 85–97.

Keegan, S.D., Mariani, N.J., Martínez, O.M., Barreto, G.F., 2005. Behaviour of smooth catalyst at high reaction rates. Chemical Engineering Journal 110, 41–56.

Mariani, N.J., Keegan, S.D., Martínez, O.M., Barreto, G.F., 2008. On the evaluation of effective reaction rates on commercial catalyst by means a one-dimensional model. Catalysis Today 133–135, 770–774.

Mariani, N.J., Mocciaro, C., Martínez, O.M., Barreto, G.F., 2009. Estimation of effectiveness factor for arbitrary particle shape and non-linear kinetics. Industrial and Engineering Chemistry Research 48, 1172–1177.

Wedel, S., Luss, D., 1980. A rational approximation of the effectiveness factor. Chemical Engineering Communications 11, 245–259.