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E. Palmisano

P. A. Ramachandran

K. Balakrishnan

M. (Muthanna) H. Al-Dahhan

*Missouri university of Science and Technology, aldahhanm@mst.edu*

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# Computation of effectiveness factors for partially wetted catalyst pellets using the method of fundamental solution

E. Palmisano, P.A. Ramachandran\*, K. Balakrishnan, M. Al-Dahhan

*Chemical Reaction Engineering Laboratory (CREL), Chemical Engineering Department, Washington University in St. Louis, One Brookings Drive, Campus Box 1198, St. Louis, MO 63130-4899, USA*

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## Abstract

Trickle bed reactors are widely used in many process industries. The catalyst particles are often incompletely wetted especially in the trickling flow regime and hence to design these reactors, the effectiveness factor of partially wetted catalyst needs to be calculated accurately. Numerical solutions by traditional methods are time consuming and not very accurate, especially for some commonly used complex catalyst shapes such as trilobes, quadrilobes etc. The paper presents a novel numerical solution for these problems based on the method of fundamental solutions. The advantage of the method is that it involves only boundary collocation and can be applied to catalysts of any shape. Further the method provides an accurate estimate of the gradient of the concentration profiles and this information can be related directly to the effectiveness factor. This accuracy of the method is demonstrated for two dimensional (2-D) and axisymmetric problems for a linear kinetics. Illustrative results are presented for some complex shapes under partial wetting conditions.

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*Keywords:* Partially wetted catalyst pellets; Trickle bed reactors; Fundamental solution

## 1. Introduction

Trickle bed reactors which are packed beds of catalyst with co-current downflow of gas and liquid, are used extensively in petroleum, petrochemical, chemical, biochemical and waste treatment processes. An example in petroleum industry is refining industry, in operations such as hydrotreating, hydrodesulfurization, and hydrodemetalization. In trickle reactors, the catalyst surface can be covered by both gas and liquid phases and this phenomenon is known as partial wetting. The partial wetting has many implications and needs to be analyzed in detail for an accurate design of these reactors. The incomplete wetting of the catalyst surface affects the conversion and also selectivities of the desired products when multiple reactions are involved. In particular, the effectiveness factor depends on the extent of wetting of

the catalyst surface. Partial wetting can increase or decrease the reaction rates depending upon the phase of the limiting reactant. Incomplete wetting of the catalyst can also result in depletion of the ‘supposedly’ abundant liquid reactant in the interior of the catalyst. Under extreme conditions for exothermic reactions one can have dryout of the catalyst interior and the phenomena is known as partial internal wetting. A number of studies have addressed various aspects of the problem (Mills & Dudukovic, 1979; Morita & Smith, 1978; Ramachandran & Smith, 1979; Herskowitz, 1981; Mills, Lai, Dudukovic & Ramachandran, 1988; Zimmerman & Ng, 1986; Ring & Missen, 1986; Tan, 1988; Al-Dahhan & Dudukovic, 1995; Tsamatsoulis & Papayannakos, 1996; Iliuta, Larachi & Grandjean, 1999; Nigam, Iliuta & Larachi, 2002).

Under milder exothermic conditions, the internal pores can be assumed to be completely filled with liquid and this represents a vast majority of industrial operations. The problem of calculation of the effectiveness factor then reduces to a numerical solution of the governing reaction–diffusion equations with non-uni-

\* Corresponding author. Tel.: +1-314-935-7187; fax: +1-314-935-7211.

E-mail address: [muthanna@wuche.wustl.edu](mailto:muthanna@wuche.wustl.edu)  
(P.A. Ramachandran).

form boundary conditions. These boundary conditions reflect the local conditions of the surface of the catalyst. Traditionally, the surface is split into a dry and wet zone, but more complicated external environments are possible. For example, even on the wetted perimeter one can have two regimes consisting of a stagnant liquid film and an actively flowing film. As a result, different mass transfer coefficients need to be imposed over the boundary. [Rajashekharam, Jaganathan and Chaudhari \(1998\)](#) modeled the hydrogenation of 2,4-dinitrotoluene considering the partial wetting and stagnant liquid holdup effects. In other words, they used a three-zone model for the external surface: one zone is dry, the other is flowing liquid and the third is stagnant liquid, with different mass transfer coefficients for each zone. In a similar way, [Ravindra, Rao and Rao \(1997\)](#) indicate that even when the catalyst is completely covered by liquid, pendular rings are formed at the contact points of the particle and the liquid flows down as thin films on the remaining surface between the pendular rings. These studies indicate the need for a detailed solution to the effect of partial wetting over the catalyst, in order to compute the effectiveness factor.

Rigorous solutions for the effectiveness factors become important in many other contexts. For example, in process such as deep hydrodesulfurization of diesel, the objective is to remove the sulfur species present in the feedstock at levels below 50 parts per million by weight (ppm by wt.). The petroleum fraction has many sulfur compounds with different reactivities, and diffusivities. As a result, there are different effectiveness factors for each sulfur compound and, the use of a single (lumped) effectiveness factor is not suitable.

In the petroleum industry, one often uses complex catalyst shapes to provide high surface to volume ratios and higher effectiveness factors ([Sie, 1993](#)) for the same catalyst loading and to minimize the pressure drop in the reactors when large amounts of catalyst are used ([Harold, 1993](#)). Examples of such catalysts are trilobes, quadrilobes, hollow cylinder etc. as shown in [Fig. 1](#), which are extensively used in hydrodesulfurization and hydrodemetallization operations. Such catalysts can be used to increase the selectivities in a reaction network when the desired product is formed in an intermediate step. When the shape of catalyst is complex (e.g. [Fig. 1](#)), one cannot determine the effectiveness factor analytically even for a first-order reaction for the case when the

surface of the catalyst is completely wetted by the liquid. The effect of partial wetting is even more important for these shape in view of the added number of contact points where pendular rings can form.

Consequently, to find accurate estimates of the effectiveness factor the diffusion-reaction equation in the catalyst particle needs to be solved numerically, with appropriate boundary conditions imposed over the surface of the catalyst. Many authors have used a variety of numerical schemes to solve the diffusion-reaction equation in a partially wetted catalyst particle. [Mills and Dudukovic \(1979\)](#) used dual and triple collocation solutions for partially wetted cylinders and spheres. For irregular geometries, the diffusion-reaction equation can be solved by the finite element method. Moreover iterative solution techniques can be used for non-linear reactions. [Zhu and Hofmann \(1997\)](#) used finite differences to evaluate effectiveness factors for Langmuir–Hinshelwood kinetics in regular geometries. However, for irregular geometries the values of concentration gradient, which is often the quantity of interest for evaluation of the effectiveness factor, can be in considerable error due to poor derivative estimates at sharp corners. The main drawback of using traditional numerical schemes such as finite elements or finite differences is that one has to discretize the entire domain of interest, which is a challenging computational task in itself, owing to the complexity of the geometry. Recently a number of mesh generation softwares have been developed which partly alleviate the problem. However, a mesh free method is still attractive especially for three dimensional (3-D) problems. Hence, the boundary element method has emerged as an alternative grid free computational technique to solve linear and non-linear diffusion-reaction equations. The use of the boundary element method for solving the diffusion-reaction problem has been demonstrated by [Ramachandran \(1991\)](#). The extension of this method to a network of multiple linear reactions has been demonstrated by [Karur and Ramachandran \(1994\)](#) where the accuracy of the method for two dimensional (2-D) problems was shown. The method has the advantage that only a boundary discretization is needed thus permitting complex geometries to be handled easily. However, the method suffers from the drawback related to the evaluation of singular integrals, which can be time consuming for irregular geometries and 3-D problems.

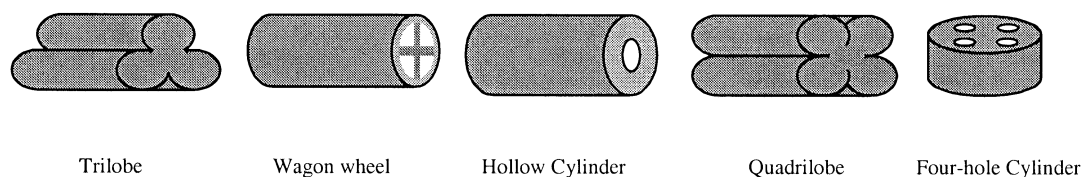


Fig. 1. Commercial complex catalyst shapes.

More recently, the method of fundamental solution (MFS), which belongs to the class of boundary methods, has shown to be a promising grid-free computational technique for solving linear partial differential equations in complex geometries with non-uniform boundary conditions. The ease and the accuracy of the MFS has been demonstrated for a number of different types of problems (such as potential field calculations, acoustics, Stokes flow etc. (for instance, see Johnston & Fairweather, 1984; Karageorghis & Fairweather, 1987; Chen, 1995). The method is useful for the solution of the catalyst effectiveness factors in trickle beds but the use of the method in this context has not been demonstrated.

The focus of this work is to demonstrate the implementation of the MFS to compute effectiveness factor for different shapes of partially wetted catalyst for a simple first order reaction. Many reactions in the industry can be approximated as first order reactions, for example, the hydrodesulfurization and hydrodenitrogenation of petroleum cuts. MFS is most efficient for first order reactions since it involves only boundary collocation as shown later in this paper. The applicability of MFS for non-linear reactions has been shown in recent studies (Balakrishnan, 2000) but the current paper focuses only on linear kinetics.

The structure of the paper is as follows; Section 2 presents the model equations. The method of fundamental solution is presented for two and 3-D geometries in Section 3. Section 4 presents some illustrative results and also shows the effect of particle shape and wetting configurations. Section 5 shows a modification of the method for axisymmetric 3-D geometries and shows how the method can be coupled to local hydrodynamic information. The next Section 6 provides the summary and conclusions.

## 2. Model equations

### 2.1. Diffusion-reaction equation for a first order reaction

The system is governed by the diffusion-reaction equation, to be solved over a domain  $\Omega$  in 2-D ( $\mathbb{R}^2$ ) or 3-D ( $\mathbb{R}^3$ ) with enclosing boundary  $\Gamma$ . For an isothermal, irreversible first order reaction, assuming that the catalyst has complete internal wetting (Mills & Dudukovic, 1979) and in steady state the equation could be written as follows:

$$D_e \nabla^2 C = kC \quad (1)$$

where,  $C$  is the concentration in the pores of the catalyst;  $D_e$ , the effective diffusivity for fully wetted catalyst;  $k$ , the first order rate constant; and  $\nabla^2$  is the Laplacian.

The general boundary condition is that of the Robin form and can be stated as follows:

$$p = \frac{\partial C}{\partial n} = \frac{k_m}{D_e} (C_b - C) \quad (2)$$

Here “ $p$ ” is the normal gradient; “ $n$ ” represents the unit outward normal from any point on the catalyst surface;  $k_m$ , the local mass transfer coefficient at that point;  $C_b$ , the concentration outside the diffusion boundary layer and  $C$  is the local concentration on the catalyst surface at that point. For the case of a partially wetted catalyst, different portions of the surface would have different values of mass transfer coefficient depending upon the local degree of wetting at that point. In other words,  $k_m$  varies along the boundary. Even for fully wetted case  $k_m$  may not be constant due to uneven liquid film thickness in the boundary. It is this non-uniformity in the boundary condition together with the complex geometry that makes the problem a computationally challenging one.

Eq. (2) covers both cases where the limiting reactant is present in either the gas phase or the liquid phase. This is achieved by assigning different values for  $k_m$  and the relevant subcases are presented below for completeness.

#### 2.1.1. Limiting reactant in the gas phase

Over the dry portion of the catalyst, the transport is relatively rapid and hence Dirichlet boundary condition can be directly used for these portion ( $C = C_b$ ). The value of  $C$  is set as  $C_b$  for these portions where  $C_b$  is now equilibrium solubility corresponding to the gas phase concentration. Over the wetted portion, where Robin boundary condition is applied, the gaseous species has to diffuse through the gas–liquid as well as the liquid–solid films and hence the value of the transfer coefficient  $k_m$  is assigned an overall value given by:

$$\frac{1}{k_m} = \frac{1}{k_{GL}} + \frac{1}{k_{LS}} \quad (3)$$

where  $k_{GL}$  is the gas to liquid mass transfer coefficient and  $k_{LS}$  is the liquid to solid mass transfer coefficient. Thus Dirichlet–Robin conditions are used for dry and wetted regions, respectively, when the limiting reactant is in the gas phase.

#### 2.1.2. Limiting reactant in the liquid phase

For a catalyst pellet partially wetted by actively flowing liquid, the value of  $k_m$  is set as  $k_{LS}$ . For the non-wetted part, the Neuman boundary condition is applicable for the case of the non-volatile limiting reactant in the liquid phase ( $\frac{\partial C}{\partial n} = 0$ ). Further simplifications can be made for large values of the mass transfer coefficient; the boundary condition simplify to the Dirichlet boundary condition on the wetted portion,

with  $C_b$  being now the bulk liquid concentration of the limiting reactant ( $C = C_b$ ).

## 2.2. Dimensionless form

The linear diffusion-reaction equation for first order reaction could be written in non-dimensional form as follows:

$$\nabla^2 c = \phi^2 c \quad (4)$$

where  $\phi$  is the Thiele modulus  $= L_C \sqrt{\frac{k}{D_e}}$ ;  $c$ , the dimensionless concentration,  $c = \frac{C}{C_b}$ ; and  $L_C$  is the

characteristic length  $= \frac{\text{Volume}}{\text{Area}}$  for complex geometries.

The operator  $\nabla^2$  in Eq. (4) is now the non-dimensional Laplacian.

For the non-volatile reactants in the liquid phase, the general Robin boundary condition can be imposed on the wetted surfaces when significant mass transfer resistances are present. This boundary condition in dimensionless form is:

$$\text{Robin: } \frac{\partial c}{\partial \zeta} = h(c - 1) \text{ over Wetted } \Gamma_1$$

where

$$\zeta = \frac{n}{L_C}$$

and  $h$  is the local Biot number  $h = \frac{k_m L_C}{D_e}$  which can be a function of surface locations for a general case.

As mentioned earlier for a catalyst pellet partially wetted by actively flowing liquid, one can impose Dirichlet boundary condition on the surface exposed to actively flowing liquid, for large values of mass transfer coefficient ( $c = 1$ ), and impose Neumann condition on the surface exposed to the gas ( $\frac{\partial c}{\partial \zeta} = 0$ ).

For gas phase limiting case we can impose the Dirichlet boundary condition on the dry surface and the general Robin condition for the wetted zone.

## 2.3. Effectiveness factor for a first order reaction

The effectiveness factor which is the primary quantity of interest of this work, is defined for a first order reaction as:

$$\eta_0 = \frac{\int_{\Omega} kC \, d\Omega}{\int_{\Omega} kC_b \, d\Omega} = \frac{\int_{\Omega} c \, d\Omega}{\Omega} \quad (5)$$

If the internal concentration field is determined (e.g. in finite element method) then Eq. (5) is the appropriate equation to use for the calculation of the effectiveness factor. In the context of MFS, an equivalent expression for the effectiveness factor (shown below in Eq. (6)) is in terms of the gradient at the surface/perimeter:

$$\eta_0 = \frac{D_e}{\Omega k C_b} \int_{\Gamma} \frac{\partial C}{\partial n} \, d\Gamma \quad (6)$$

In non-dimensional form Eq. (6) could be written as follows:

$$\eta_0 = \frac{1}{\Omega^* \phi^2} \int_{\Gamma^*} \frac{\partial c}{\partial \zeta} \, d\Gamma^* \quad (7)$$

where  $\Omega^*$  and  $\Gamma^*$  are defined as  $\Omega^* = \frac{\Omega}{L_C^2}$  and  $\Gamma^* = \frac{\Gamma}{L_C}$

for 2-D geometries or  $\Omega^* = \frac{\Omega}{L_C^3}$  and  $\Gamma^* = \frac{\Gamma}{L_C^2}$  for 3-D geometries.

## 3. The method of fundamental solution (MFS) for linear diffusion-reaction equations

The method of fundamental solution (also called the source superposition method) belongs to the class of boundary methods. Here one seeks solutions, which satisfy the differential equation exactly in the interior but not the boundary. This results in a residual error on the boundary. This error is made to be zero at selected collocation points (or in a least square sense for a more general variation of the source method). In this work we use the boundary collocation technique to solve the problem based on the work presented by Balakrishnan and Ramachandran (2000). Thus the first task is to look for the general solution to the differential equation. These general solutions are known as the fundamental solution to the governing partial differential equation. These solutions are applicable at all points on an infinite domain except at a point where the solution has a singularity. Details are presented below.

The differential operator corresponding to the Eq. (4) has a fundamental solution  $G$  satisfying:

$$\nabla^2 G - \phi^2 G = -\delta(r) \quad (8)$$

where  $-\delta(r)$  denotes a source of unit strength at the origin and  $r$  is the (scaled) distance at any point from the origin. The solution to Eq. (8) is the fundamental

solution in two dimensions for the diffusion-reaction problem and is given by:

$$G = \frac{1}{2\pi} K_0(\phi r) \tag{9}$$

where  $K_0$  is the modified Bessel function of the second kind.

Similarly in three dimensions, the fundamental solution can be derived as:

$$G = \frac{\exp(-\phi r)}{4\pi r} \tag{10}$$

If the source is not located at the origin but at a point  $(x_i, y_i)$  then the fundamental solution  $G_i$  is given by:

$$G_i = \frac{1}{2\pi} K_0(\phi r_i) \tag{11}$$

where  $r_i$  is the distance between the source point  $(x_i, y_i)$  and any field point in the domain or on the boundary.

Assume that the source point is located outside the domain  $\Omega$ , then the fundamental solution  $G_i$  satisfies the governing Eq. (4) in the interior of the domain in an exact sense, but not any particular set of boundary conditions. In order to satisfy the boundary conditions we choose a set of basis solutions and use these to construct an approximation for “ $c$ ”. Thus we can reconstruct the solution “ $c$ ” by a set of functions  $G_i$  obtained by placing ‘ $n$ ’ distinct source points outside  $\Omega$ . Such solution is represented as:

$$c = \sum_{i=1}^n a_i G_i \tag{12}$$

where  $a_i$  ( $i = 1$  to  $n$ ) are the set of unknown coefficients which will be determined in order to satisfy the boundary conditions. To determine the coefficients  $a_1 - a_n$  we choose  $n$  field points on the domain boundary, collocation points, and  $n$  source points outside the domain to set up a system on  $n$  linear equations in as many unknown ( $a_i$ ). Thus applying the boundary collocation condition on Eq. (12) one obtains for 2-D the following equation:

$$c_k = \sum_{i=1}^n \frac{a_i}{2\pi} K_0(\phi r_{ik}) \tag{13}$$

where  $c_k$  is the specified concentration value at the  $k$ th collocation point for a purely Dirichlet problem, and  $r_{ik}$  is the Euclidian distance between the  $k$ th point on the boundary and the  $i$  source point outside the domain.

When a collocation point is located on part of the boundary where Neumann condition is imposed Eq. (13) is replaced by the following equation which follows by taking the normal derivative of Eq. (12).

In two dimension:

$$\left(\frac{\partial c_k}{\partial \zeta}\right)_{x=x_k} = - \sum_{i=1}^n \frac{a_i}{2\pi r} K_1(\phi r_{ik}) \times [(x_k - x_i)n_x + (y_k - y_i)n_y] \tag{14}$$

where  $K_1$  is the modified Bessel function of the second kind and order 1.

Similarly, for 3-D problems we have the following equation at the Neumann points:

$$\left(\frac{\partial c_k}{\partial \zeta}\right)_{x=x_k} = - \sum_{i=1}^n \frac{a_i}{2\pi r_i^3} \times (1 + \phi r_i \exp(\phi r_i) \times [(x_k - x_i)n_x + (y_k - y_i)n_y + (z_k - z_i)n_z]) \tag{15}$$

$n_x, n_y$  and  $n_z$  are the component of the unit normal to the perimeter/area in 2-D/3-D in the coordinate directions.

For more general boundary condition of the Robin types, the solution  $c_k$  can be handled in a similar manner with the following:

$$c_k = \sum_{i=1}^n a_i \left( \frac{1}{h} \frac{\partial G_i}{\partial \zeta_k} + G_{ik} \right) \tag{16}$$

We can use the expression of the flux to evaluate the effectiveness factor (Eq. (6)) because it only requires knowing the normal gradient at the boundary. This is given by:

$$\frac{\partial c}{\partial \zeta} = \sum_{i=1}^n a_i \frac{\partial G_i}{\partial \zeta} \tag{17}$$

The discretization form of the effectiveness factor (Eq. (7)) using Gaussian quadrature is given by:

$$\eta_0 = \frac{1}{\Omega^* \phi^2} \sum_{k=1}^n W_k \frac{\partial c}{\partial \zeta_k} \tag{18}$$

where  $W_k$  denotes the Gaussian weights associated with each collocation point in the numerical integration procedure used to find  $\eta_0$ .

The solution procedure using the MFS is thus extremely simple. Once chooses a set of ‘ $n$ ’ collocation points on the boundary and a set of ‘ $n$ ’ source points outside the domain. For each boundary point the appropriate prescribed boundary condition is applied. For example, Eqs. (13) and (14) or Eq. (16) applies in 2-D depending on the whether point has a Dirichlet, Neumann or Robin boundary conditions. The resulting sets of  $n$  linear algebraic equations are solved for the coefficients  $a_i$ . The gradient at each point is then available directly from Eq. (17) and the effectiveness factor can be calculated from Eq. (18). The concentra-

tion profiles in the interior can also be readily calculated using the boundary fitting coefficients,  $a_i$ . Thus, Eq. (12) provides directly an empirical analytical concentration profiles in the interior as well. This is one of the advantage of the MFS method in contrast to the classical boundary element method.

The accuracy depends on the location of the collocation and source points and in this work some trial and error has been performed to adjust the distance between them. The accuracy can be judged by the boundary residuals. Thus the boundary values are back calculated after calculating the coefficients  $a_i$  and compared with the prescribed values. If the sum of the residual error is small then the calculated solutions represent an almost exact solution to the problem. Often the fitted errors can be within the machine single precision ( $10^{-5}$ ) resulting in an accurate solution for any complex geometry.

In order to standardize the location of the collocation and source points, Balakrishnan and Ramachandran (2000) suggested the following heuristic procedure (a more precise method based on statistical analysis of the result is being undertaken and is not presented here). The heuristic rule is that the source points are chosen outside the perimeter such that the ones adjoining the Neumann or Robin boundaries are closer to the perimeter than those adjoining the Dirichlet boundaries. The collocation points are placed at the roots of the Jacobi polynomials. Such a location of the collocation points permit avoid geometric singularities like sharp corner and singularities at the boundary conditions, e.g. the junction between Dirichlet and Neumann boundary conditions. A typical placement of the collocation points and source points by this method is shown in Fig. 2.

#### 4. Test cases and results

In this section, we present some test cases to demonstrate the efficacy of the MFS for evaluation of the effectiveness factors of regular and non-regular catalyst shapes under different wetting environments using the above-discussed methodology. We consider some cases with regular catalyst shapes and wetting environments where analytical or prior numerical solutions are available. This is followed by demonstration of the method for complex catalyst shapes used in industry. Also some results regarding the effect of wetting configuration are presented.

Illustrative results for 2-D are now presented. The calculations for 3-D follow similar lines, thus the same code can be used for 2-D and 3-D. The 3-D results are not shown here for brevity. However, many 3-D problems can be simplified further if there exists axisymmetry. This requires a modification to the 2-D fundamental solution. This refinement and the results for axisymmetric cases are presented in Section 5.

##### 4.1. Square and circular geometries

In this section, we compute the values for the effectiveness factor for two problems. For the first problem we solve the diffusion-reaction equation at different wetting conditions (i.e. different values of wetting efficiency,  $f$ ) for two types of geometries, a square slab and infinite cylinder (which can be represented as a circle in 2-D). The square and the circle cases are solved for two values of Thiele modulus ( $\phi = 1$  and 10) under liquid limiting condition, with boundary condition of Dirichlet for the wetted surface and

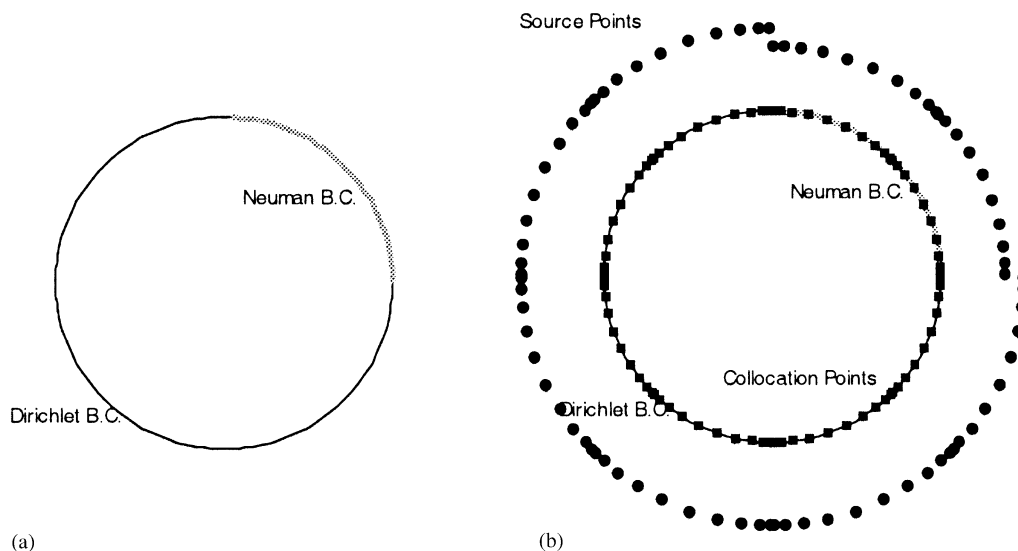


Fig. 2. (a) Circle problem; (b) collocation and source points placement.

Neumann for the dry surface. The second problem for circle is solved for two values of Thiele modulus ( $\phi = 2$  and 20), under liquid limiting condition, with boundary condition of Robin for the wetted surface and Neumann for the dry surface.

The results of solving these problems are presented in Figs. 3–5. In Fig. 3, we compare the effectiveness factors obtained using the MFS with those obtained by Mills and Dudukovic (1979) for a slab geometry. The wetting configurations used for this case is shown in Fig. 3A. The results obtained by MFS show a good agreement with those obtained by Mills and Dudukovic (1979). The relative difference between these effectiveness factors is less than 2%. Fig. 4 shows the corresponding results for a cylinder. The geometry and wetting configuration used for this computation is shown in Fig. 4a. The results are shown for two Thiele moduli of 1 and 10 and agree well with that generated by Mills and Dudukovic by dual series expansion method. In Fig. 5 we compare the effectiveness factors for an infinite cylinder computed using the MFS, with those obtained by Herskowitz (1981). The parameter values used for this case are marked in Fig. 5 and the wetting configuration used is shown in Fig. 5a. The results as well show a good agreement between the MFS and Herskowitz (1981) values, with relative difference less than 5%.

This indicates the usefulness of the code for the Robin type of boundary conditions on the wetted perimeter.

#### 4.1.1. Effect of wetting environment

The effect of wetting configuration has been studied in this work for slab geometry, for two different Thiele modulus ( $\phi = 1$  and 10). Fig. 6 shows five different wetting configurations for the same wetting factor (50%) and the corresponding the results for the effectiveness factors are reported in Table 1. We can see that for the same wetting efficiency, the wetting configurations do affect the effectiveness factor, with relative differences of the order of 7 and 16%. The differences are more pronounced at higher values of the Thiele modulus. These trends are in agreement with Capra, Sicardi, Gianetto and Smith (1982).

We can visualize this effect for a large Thiele modulus as follows. The effectiveness factor for 2-D geometry is proportional to the area of the concentration boundary layer over the total area of the particle. If we perform a dimensional analysis, the boundary layer concentration has a thickness, which is order of  $1/\phi$ . If the boundary layer overlaps (such as a corner of a slab) then the reaction area is reduced leading to a reduction in the effectiveness factor. There is a further contribution to the effectiveness factor from the extra transport due to

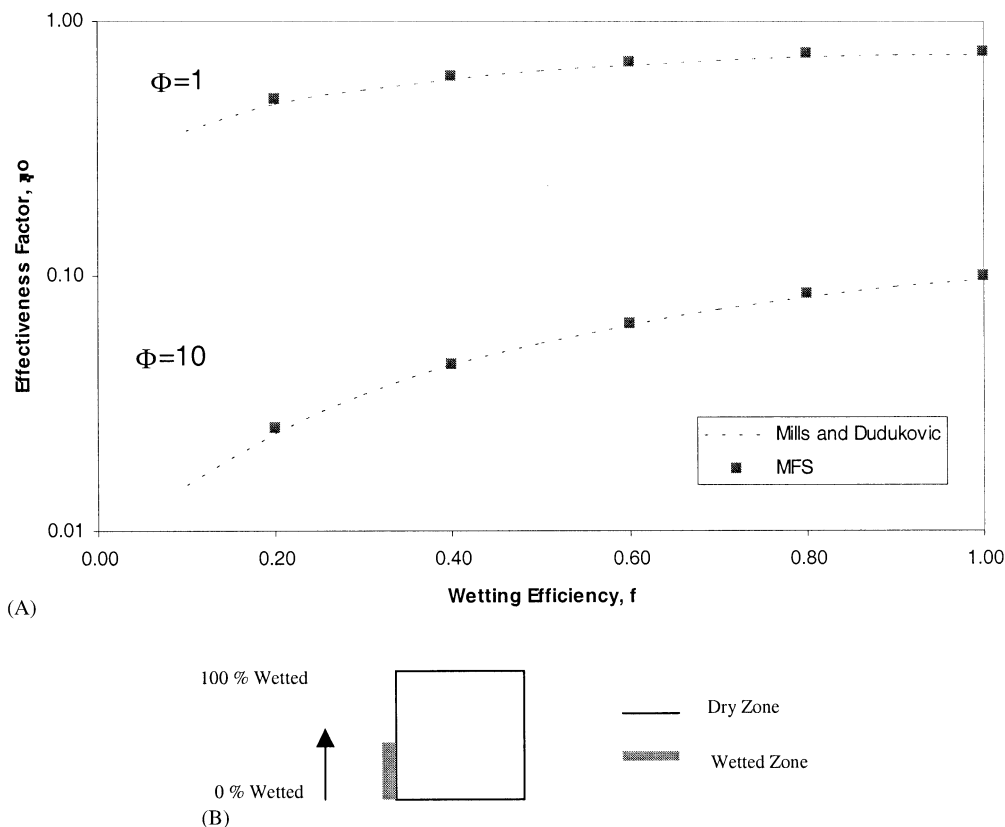


Fig. 3. (A) Comparison between the effectiveness factors obtained for a slab using MFS with those obtained by Mills and Dudukovic (1979). (B) Wetting environment used by Mills and Dudukovic (1979) for slab.



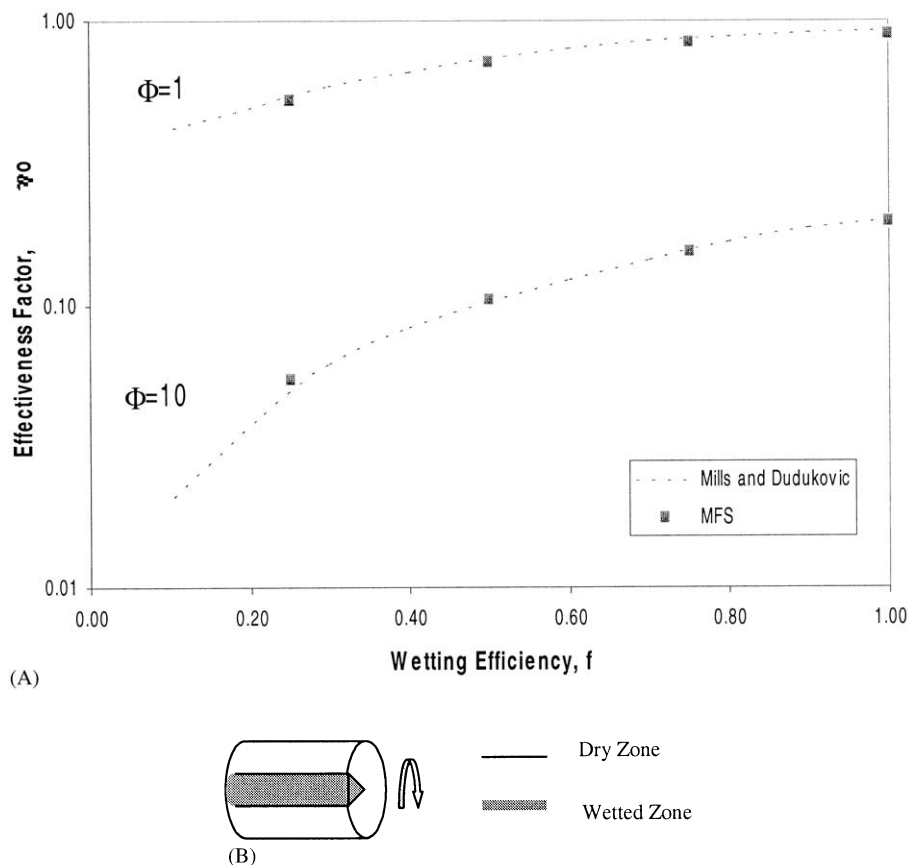


Fig. 4. (A) Comparison between the effectiveness factors obtained for an infinite cylinder using MFS with those obtained by Mills and Dudukovic (1979). (B) Wetting environment used by Mills and Dudukovic (1979), for a cylinder.

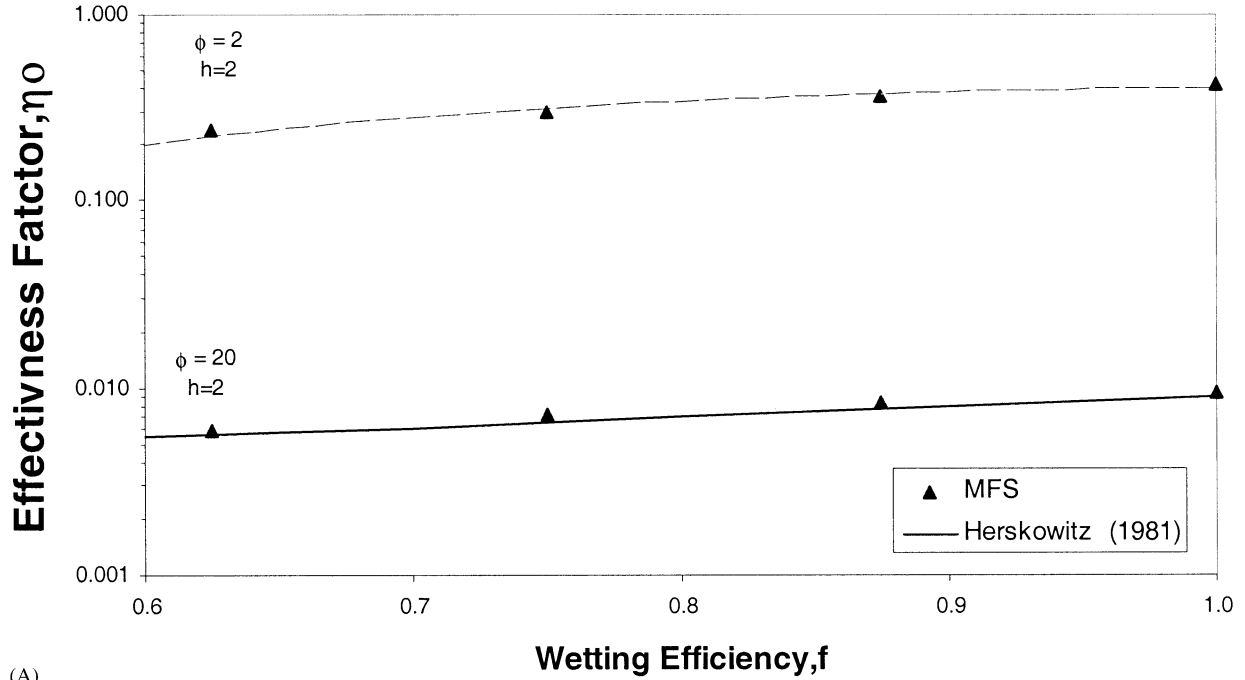
the higher lateral diffusion at region where there is a change in boundary condition from wetted (Dirichlet) to dry (Neumann) perimeter. These points are referred to as the region of singularity (see Fig. 6A). The combination of the two factors (overlapping of the boundary layer and singularity regions) determine the magnitude of the effectiveness factor. The results of Table 1 can be rationalized based on these ideas as discussed below.

Configuration 1 has the maximum effectiveness factor, because there are four-wetted zone which contribute to the boundary layer concentration; in addition, this configuration has four singularity points, (as indicated in Fig. 6A) when the wetted zone change to dry zone, generating an additional lateral diffusion. For configuration 2, the wetted zone contributes in the same way that configuration 1 but this configuration does not have any singularity point; as a result, the effectiveness factor is lower as compared with configuration 1 (see Table 1). For configuration 3 there is an overlapping in the boundary layer zone, which means that the reaction area has a common portion that can be only accounted for one time, which reduce the effectiveness factor, but this configuration has two singularity points which increase  $\eta_0$ . The overlapping region has a larger reduction to the effectiveness factor (reducing effect) than the

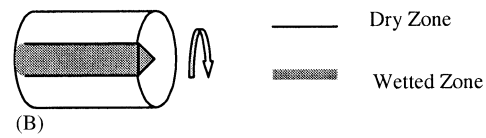
singularly points. Therefore, the effectiveness factor for configuration 3 is lower than the configurations 2 and 1 (Table 1). Configuration 4, there is only one overlapping in the boundary layer zone and no singularity contributions; therefore, a lower effectiveness factor is expected. As compared with configuration 1, 2 and 3 (Table 1), the last configuration studied in this work (configuration 5) has two overlapping in the boundary layer zone, but with two singularities points. This has, the lowest effectiveness factor of all the cases. However, the difference in configuration 4 and 5 is not significant. The above physical interpretation provides an explanation to the configurational effects reported in earlier studies (Capra et al., 1982).

#### 4.2. Non-regular two-dimensional geometry

In order to evaluate the effectiveness factor for complex geometries we solve the reaction-diffusion equation, for a first order reaction (Eq. (4)), for trilobe and quadrilobe geometries, under different wetting environment with liquid limiting condition, over a range of Thiele moduli. For this problem we assume Dirichlet boundary condition for the wetted zone ( $c = 1$ ) of the

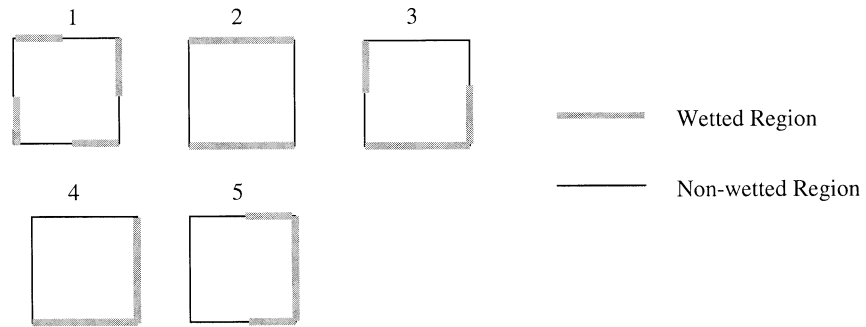


(A)

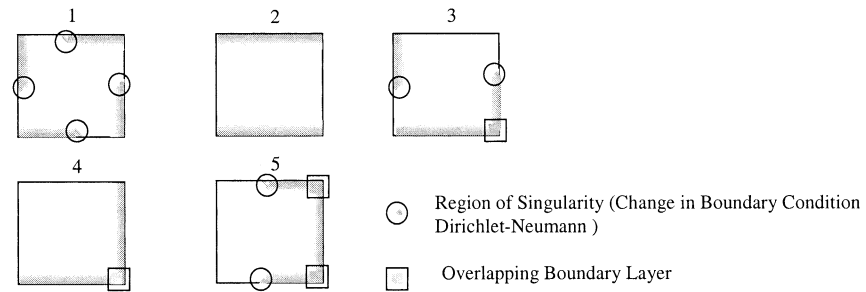


(B)

Fig. 5. (A) Comparison between the effectiveness factors obtained for an infinite cylinder using MFS with those obtained by Herskowitz (1981). (B) Wetting environment used by Herskowitz (1981) for a cylinder.



(A)



(B)

Fig. 6. (A) Different wetting configuration, for a slab. (B) Different boundary layer for a slab geometry.

Table 1  
Effectiveness factor, for different wetting configurations shown in Fig. 6

Configuration	Effectiveness factor $\eta_0$	
	$\phi = 1$	$\phi = 10$
Configuration 1	0.9433	0.2204
Configuration 2	0.9242	0.2000
Configuration 3	0.9098	0.1977
Configuration 4	0.8821	0.1873
Configuration 5	0.8761	0.1851

The wetting efficiency is 50% for each case.

particle and Neumann boundary condition for the dry zone ( $\frac{\partial c}{\partial \zeta} = 0$ ).

For these geometries there are no results available in the literature for comparison of the accuracy of MFS. Therefore, we solve the problem using two different numerical methods, the first is the MFS, and the second method is the finite element method using the software FEMLAB<sup>®</sup>. The results of the two problems are presented in Figs. 7 and 8. It is obvious there is not significant deviation between the values of the effectiveness factors obtained by the two methods (the relative difference less than 5%). The finite element method requires a domain discretization and is more difficult to use. The gradients are not directly obtained in the finite element method and this can contribute an additional

source of error. Also for large Thiele modulus, the finite element method requires a fine meshing of the boundary layer and the accuracy is less for these cases compared with MFS. Also the speed of calculation depend on the Thiele modulus when finite elements are used in view of fine meshes needed in the boundary layer but is independent of Thiele modulus for MFS since only boundary collocation is used. Computation times using MFS are lower by about one third for 2-D problems and is expected to be even lower for 3-D problems.

Fig. 9 presents the effectiveness factors, for cylinder, trilobes and quadrilobes geometries, under liquid limiting condition for various wetting environments, computed by the MFS. These are compared with the generalized solution in this figure. The generalized solution is defined as the analytical solution of the effectiveness factor for slab geometry. We can see that for higher Thiele modulus the use of the generalized solution gives a good approximation for the effectiveness factors for a cylinder, as was showed by Mills and Dudukovic (1979), even for complex geometries such as the trilobe and quadrilobe, with relative error of 10%. The reason for this is the fact that the diffusion boundary layer is thin for higher values of Thiele modulus and the curvature effects are not significant. Hence a slab model (the basis of generalized Thiele modulus) is a good approximation to these cases. Fig. 9 also shows the effect of the geometry on the effectiveness factor. It is clear that for the same Thiele modulus,

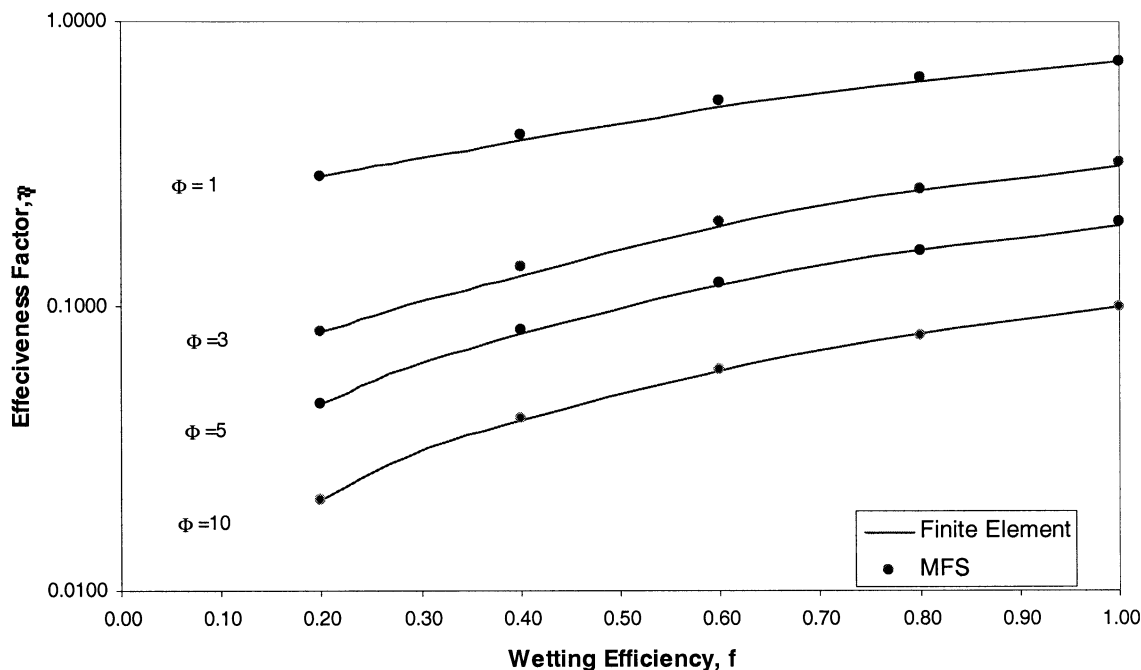


Fig. 7. Comparison between the effectiveness factors obtained for a trilobe using MFS with those obtained using finite element method under liquid limiting conditions.

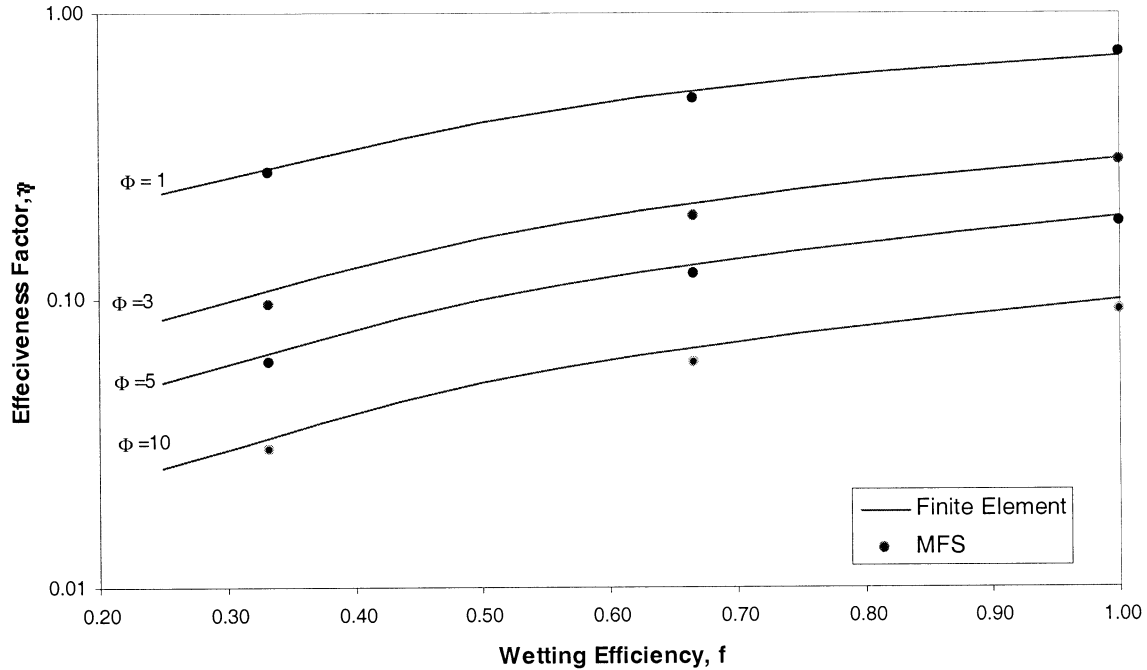


Fig. 8. Comparison between the effectiveness factors obtained for a quadrilobe using MFS with those obtained using finite element method under liquid limiting conditions.

higher effectiveness factor is obtained using slab geometries. However, the differences in cylinder, trilobe and quadrilobe geometries are not significant. The differences are, however, significant for lower Thiele modulus as seen in Fig. 9 for  $\phi = 1$  and for these cases MFS method is preferable.

### 5. 3-D axisymmetric bodies

For a simple catalyst shape such as finite cylinders and spheres, which are axisymmetric one can consider the wetting also axisymmetric. This greatly simplifies the problem since we can use an axisymmetric fundamental

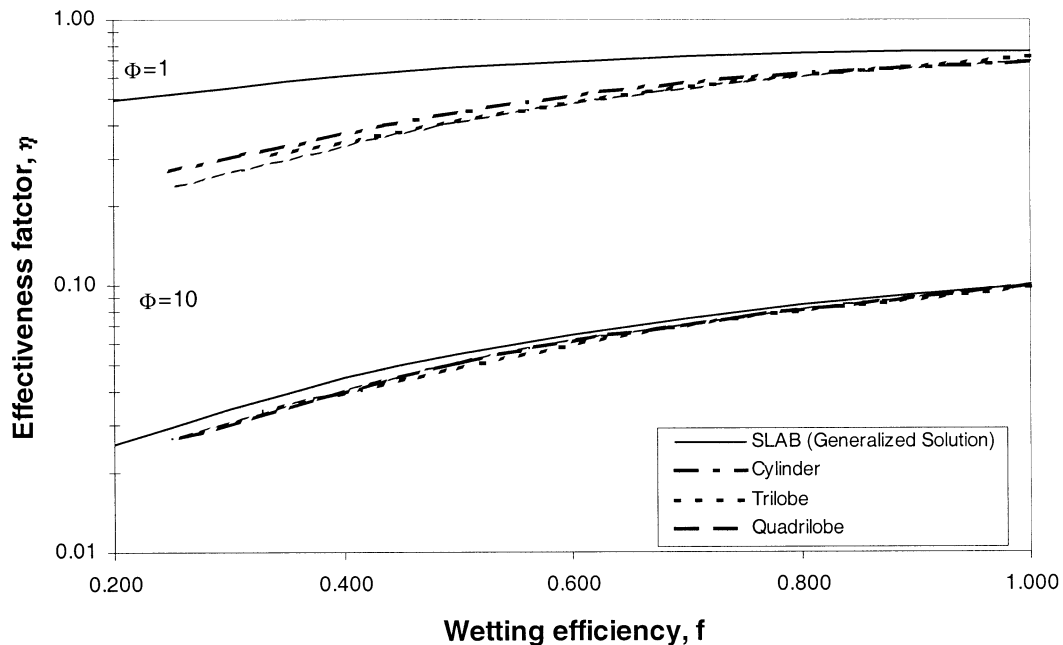


Fig. 9. Comparison between the effectiveness factors obtained for different geometries using MFS and those obtained by generalized Thiele modulus at various wetting environment under liquid limiting.

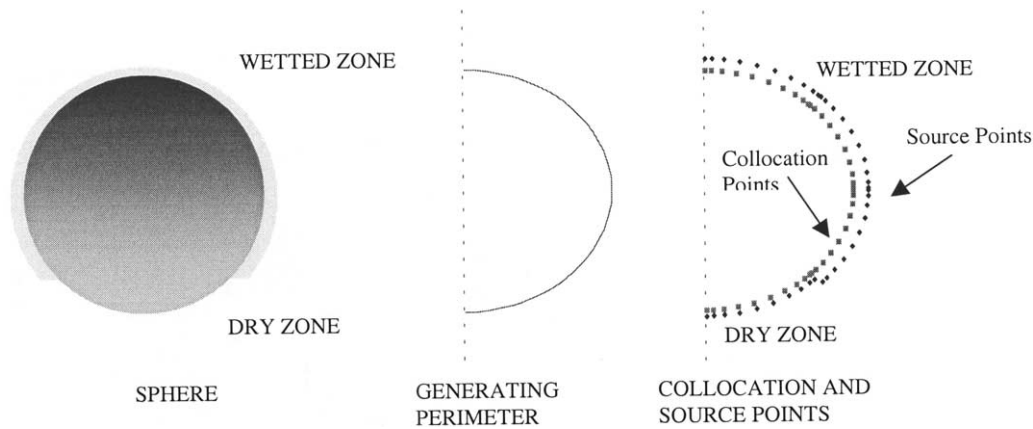


Fig. 10. Axisymmetric problem for a sphere.

solution, which reduces the dimensionality of the problem. A 3-D axisymmetric body can be constructed by rotation of a generating perimeter placed in a 2-D plane (the generating plane); see Fig. 10 for an illustration.

Consider a source point  $(r_i, z_i)$  located in the generating plane and a variable point  $(r, z)$  on the surface or interior of the catalyst. Then the fundamental solution for the axisymmetric case is obtained by integrating the fundamental solution to the 3-D diffusion-reaction equation in the azimuthal ( $\theta$ ) direction over the range of  $0-2\pi$  (Karageorghis & Fairweather, 1999). Thus the axisymmetric fundamental solution is given by:

$$G_i = \int_0^{2\pi} \frac{\exp(-\phi\rho_i)}{4\pi\rho_i} d\theta \quad (19)$$

Eq. (19) corresponds to the fundamental solution to a ring source around the catalyst where  $\rho_i$  is defined as:

$$\rho_i = \sqrt{r_i^2 + r^2 + (z_i - z)^2 - 2rr_i \cos \theta} \quad (20)$$

The normal gradient of the fundamental solution is given by:

$$\frac{\partial G_i}{\partial \zeta} = \int_0^{2\pi} \frac{\exp(-\phi r_0)(1 + \phi r_0)}{4\pi\rho_i^3} \times [(r_i \cos \theta - r)n_r + (z_i - z)n_z] d\theta \quad (21)$$

with  $G_i$  and  $\frac{\partial G_i}{\partial \zeta}$  defined as above. Note that the axisymmetric fundamental solution cannot be obtained in closed form unlike the 2-D and 3-D equations presented earlier. The solution is now an integral along  $\theta$  (Eq. (19)) and is evaluated by Simpson rule.

For axisymmetric bodies we can define the effectiveness factor as follows:

$$\eta_0 = \frac{2\pi}{\Omega^* \phi^2} \sum_{i=1}^n W_i r_i \frac{\partial c}{\partial n_i} \quad (22)$$

where  $r_i$  is the distance between the collocation points and the revolution plane.

### 5.1. Results for axisymmetric geometry

Results for a sphere are presented using the axisymmetric fundamental solution. A sphere can be obtained by rotation of a semicircle in 2-D as shown in the Fig. 10. Collocation points are placed on the semicircle and source points on a larger semicircle (Fig. 10). Note that the points should not be placed on the axis of symmetry. For this problem we computed the effectiveness factor at different values of wetting efficiency,  $f$ , for a sphere, under liquid limiting condition, using boundary condition of Dirichlet for the wetted surface and Neumann for the dry surface for different Thiele moduli. The results of these problems are presented in Fig. 11. The figure shows that for sphere geometry, the solution using MFS fit very well the solution for the effectiveness factor presented by Mills and Dudukovic (1979) with relative difference less than 8%.

In order to show the effect of the different mass transfer coefficient along the surface, we consider the case for a fully wetted sphere (radius = 1) with a two different Thiele modulus (1 and 10), where the mass transfer coefficient is not uniform, and varies with the angle  $\Psi$  (non-uniform Robin boundary condition). We assume that the mass transfer coefficient is maximum at the North pole of the sphere, and is minimum at the South pole. The values of the Biot number used have a maximum of 1 at the North pole and 0.1 minimum at the South pole. We compare the effectiveness factor computed using this configuration, with these computed using the average Biot number of 0.55. The values of the effectiveness factor using varying Biot number are 0.59 and 0.0155 for Thiele modulus of 1 and 10, respectively. The effectiveness factors using the average value of

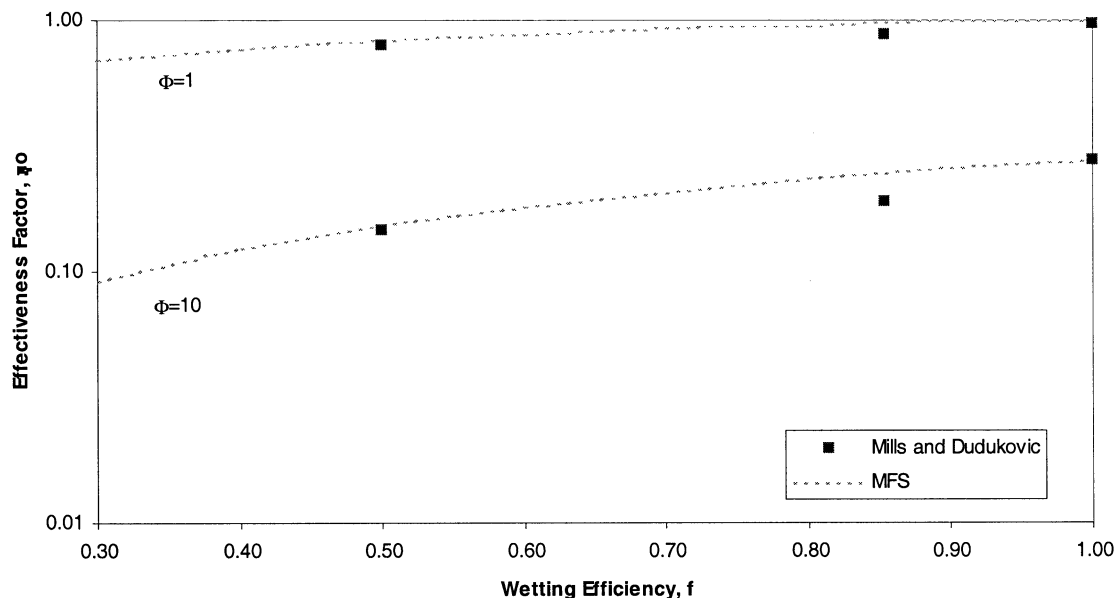


Fig. 11. Comparison between the effectiveness factors obtained for a sphere using MFS with those obtained by Mills and Dudukovic (1979) under liquid limiting conditions.

Thiele modulus are 0.60 and 0.0157, respectively. As we can see there is not significant difference (< 3%) between the effectiveness factor using an average value of Biot number, and the effectiveness factor computed using a detailed Biot number variation. This result indicates that we can use an average values of Biot number in order to compute effectiveness factor. This finding cannot, however, be generalized to non-first order reaction, which will be examined in a separate study.

## 6. Conclusion remarks and future extensions

The primary objective of this work is to demonstrate the use of the source method also known as the MFS for evaluation of the effectiveness factors for a first order reaction in complex catalyst geometries under different wetting environments encountered typically in trickle bed reactors. The accuracy of the method has been validated using existing numerical solutions for regular catalyst shapes and the efficacy of the method for complex catalyst shapes has been demonstrated under a plethora of wetting conditions. The simplicity of the method provides for rapid evaluation of effectiveness factors for linear reaction without considerable computational effort in both 2-D and 3-D. The grid-free nature of the scheme completely circumvents the efforts of grid generation required for complex catalyst geometries when using other methods. Though the method has been only demonstrated to be applicable for a first order reaction, an analogous method based on a matrix of particular solutions can be developed for non-linear

reactions. Another approach for non-linear reactions is that of quasilinearization over subdomains demonstrated by Kasab, Karur and Ramachandran (1995) for moderate Thiele moduli, wherein bounds on the effectiveness factor can be determined within respectable limits. The advantage of such an approach is that the method still requires only discretization of the perimeter (or the boundary in 3-D) and permits rapid evaluation of the effectiveness factor. The extensions to non-linear reactions by quasilinearization and for multiple reactions will be reported in a future communication.

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