

A GRAIN MODEL FOR CATALYST TORTUOSITY

TIMUR DOĞU

*Department of Chemical Engineering
Middle East Technical University
Ankara, Turkey*

and

GÜLŞEN DOĞU

*Department of Chemical Engineering
Gazi University
Ankara, Turkey*

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A simple model was proposed for the prediction of tortuosity factor of porous solids with mono or bidispersed pore size distributions. Model predictions were presented in graphical form for quick estimation of tortuosity. The experimental tortuosity factors reported in the literature for porous solids of different pore structures and the corresponding predicted values showed good agreement.

KEYWORDS Grain model Catalyst Tortuosity.

INTRODUCTION

The mechanism of mass transport within a porous solid is rather complex and depends on the nature of pore structure. The geometry of pores are usually irregular. The prediction of effective diffusion coefficient requires information on the pore size distribution and the tortuosity of the porous catalyst. A detailed review of diffusion of gases in porous solids was reported by Youngquist (1970). Scott and Dullien (1962), Evans *et al.* (1961), Wakao *et al.* (1965) derived diffusion equation in capillaries considering the combined effect of molecular and Knudsen diffusion modes. Doğu (1986) reported a summary of diffusion models and experimental techniques to determine diffusivities in porous catalysts.

Several models are proposed in the literature for the description of diffusive fluxes in porous solids. The random pore model of Wakao and Smith (1962, 1964) is proposed for predicting diffusion rates at constant pressure through a bidisperse porous media. In this model, diffusion through the pellet is considered to take place by three parallel paths, namely through macropores, through micropores and through macro and micropores in series. It was assumed that flux through macropores is proportional to the square of macroporosity. In the model proposed by Johnson and Stewart (1965), the diffusion rate through the porous

solid is predicted by the integration of diffusion rate in capillaries over the whole pore size distribution and a tortuosity factor of 3 was recommended. Considering converging and diverging pores, Foster and Butt (1966) proposed another diffusion model for isobaric binary mixtures. Recently Carniglia (1986) proposed another model which allows prediction of tortuosity from detailed pore size distribution data together with BET surface area values. Procedure requires lengthy calculations and it is necessary to estimate the pore shape factors from extended porosimetry and surface area data.

Diffusion in porous solids was also studied by Feng and Stewart (1973) and Patel and Butt (1975). Pekula and Greenkorn (1971) reported an experimental study for the investigation of porous medium with non-uniform pores. Klusacek and Schneider (1981a,b) investigated multicomponent diffusion and shape factors on effective diffusion in porous solids. Satterfield (1970) reviewed transport in porous media and reported considerable amount of data in his fine book.

Satterfield and Caddle (1968) reported totuosity factors obtained from steady state diffusion experiments in commercially manufactured pelleted catalysts. Their results show that tortuosity factors are between 3 and 7.

It is generally believed that the prediction of effective diffusion coefficients, by the integration of $D_T(r)$ over the pore size distribution would give satisfactory estimates (Wang and Smith, 1983).

$$D_e = \frac{1}{\tau} \int_{a_0}^{\infty} D_T(r) f(r) dr = D_T \frac{\varepsilon}{\tau} \quad (1)$$

where

$$D_T(r) = 1/[(1 - \alpha y_A)/D_{AB} + 1/D_{KA}]. \quad (2)$$

For the prediction of D_e from Eq. (1), some researchers considered the whole pore size distribution including micropores. On the other hand, in some other publications, the major contribution to diffusion flux was considered to be in macropores and lower limit of integral was chosen as a characteristic radius separating micro and macropores. Consequently, the tortuosity factors estimated using total and macro pore size distributions differ.

Many catalyst pellets are made by the agglomeration of microporous grains. Such catalysts have bidispersed pore structure. Macropores are formed between the agglomerated grains. Transport of species in such catalysts is generally represented by two species equations, one in the microporous particle and the other for the macropore region of the pellet. It was shown by Örs and Doğu (1979) that, for such catalysts the effectiveness factor is a function of dimensionless group α and particle Thiele modulus. The magnitude of α is proportional to the ratio of diffusion times in the macro and micropore regions.

In this work, using the pellet-grain representation of a porous catalyst, a simple model was proposed for the prediction of tortuosity factor. It was also shown that information about macroporosity is enough for this prediction in many cases.

Modelling of Tortuosity

In the development of the model, a unit cell of the catalyst pellet was defined as the smallest element representing the pore structure of the pellet. This unit cell is

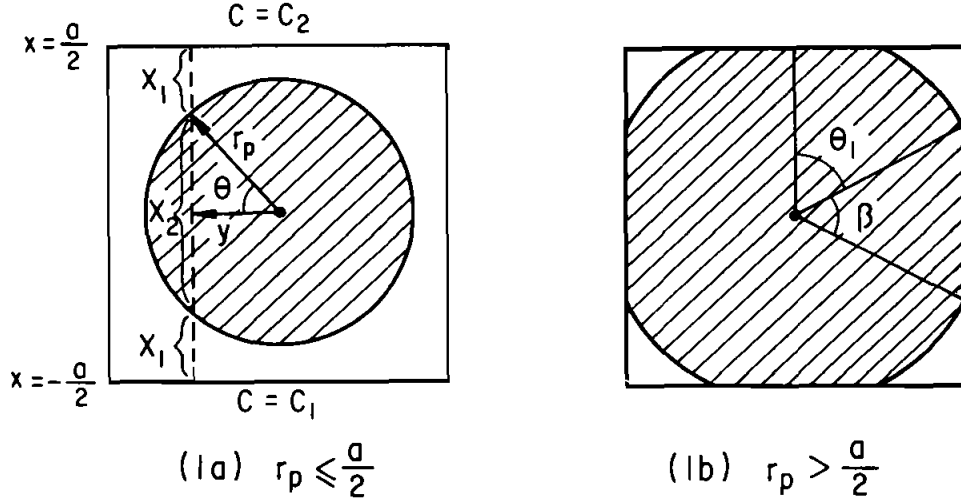


FIGURE 1 Presentation of unit cell of the grain.

considered to contain a single grain of radius r_p (Figure 1a). The void volume outside the grain is considered as macropore. If there are micropores within the grain, then the catalyst was considered to have a bidispersed pore structure. Macroporosity of the pellet is then expressed as

$$\varepsilon_a = 1 - \frac{4}{3} \pi \left(\frac{r_p}{a} \right)^3, \quad \text{for } r_p \leq \frac{a}{2} \quad (3)$$

Considering one dimensional diffusion, the effective concentration gradient in the unit cell was taken as $\frac{dC}{dx} = \frac{C_2 - C_1}{a}$. The concentrations at $x = -a/2$ and at $x = +a/2$ (C_2 and C_1) were considered to be independent of y within the cell. Diffusion flux through the unit cell was then expressed as,

$$N_e = - \left[D_{T_s} \left(1 - \pi \left(\frac{r_p}{a} \right)^2 \right) + 2\pi \int_0^{r_p/a} \left(\frac{1}{\frac{x_2}{aD_i} + \frac{2x_1}{aD_{T_s}}} \right) \left(\frac{y}{a} \right) d \left(\frac{y}{a} \right) \right] \frac{dC}{dx} = - D_e \frac{dC}{dx} \quad (4)$$

On the right hand side of this expression, the first term corresponds to the diffusion in the macropore (void space outside the grain) while the second term (integral expression) corresponds to series contribution through macro and micropores. Taking $y = r_p \cos \theta$, $x_2 = 2r_p \sin \theta$ and $x_1 = (a - x_2)/2$ integration is carried out. Expressing effective diffusivity in terms of macroporosity as $D_{e_A} =$

$D_{T_s} \frac{\varepsilon_a}{\tau_a}$, tortuosity factor based on macroporosity was expressed as

$$\frac{\varepsilon_a}{\tau_a} = 1 - \pi \left(\frac{r_p}{a} \right)^2 + \pi \frac{\left(\frac{r_p}{a} \right)}{\left(\frac{D_{T_s}}{D_i} - 1 \right)} \left[1 - \frac{\ln \left(1 + 2 \frac{r_p}{a} \left(\frac{D_{T_s}}{D_i} - 1 \right) \right)}{2 \frac{r_p}{a} \left(\frac{D_{T_s}}{D_i} - 1 \right)} \right] \quad (5)$$

(for $r_p \leq \frac{a}{2}$ which corresponds to $\epsilon_a \geq 0.476$).

The order of magnitude of D_i was reported to be in the range of 10^{-4} – 10^{-6} cm²/s (Hashimoto and Smith, 1973, 1974; Doğu and Ercan, 1983) while the order of magnitude of effective macropore diffusion coefficient is 10^{-2} cm²/s (Doğu, 1986). Estimating the order of magnitude of D_{T_e} as 10^{-1} it wouldn't be erroneous to say that for most practical problems the order of magnitude of D_{T_e}/D_i is greater than 10^3 . For such cases the order of magnitude of third term in Eq. (5) becomes negligible. This corresponds to neglecting series diffusion contribution of macro and micro pores to the total flux which is a reasonable assumption for pellets with large macroporosity. This result is consistent with the assumption of grain-pellet approach proposed in the literature for the bidisperse porous catalysts. For the case of negligible contribution of micropore diffusion to the net flux through the pellet, the tortuosity factor expression becomes a function of macroporosity only.

$$\tau_a = \frac{\epsilon_a}{1 - \pi \left[(1 - \epsilon_a) \frac{3}{4\pi} \right]^{2/3}}, \quad \text{for } \epsilon_a \geq 0.476. \quad (6)$$

For a pellet with a macroporosity smaller than 0.476, effective particle diameter becomes larger than cell size ($r_p > \frac{a}{2}$). As shown in Figure 1b, for such pellets the volume of nonspherical grain can be written as

$$V_{\text{grain}} = \frac{4}{3}\pi r_p^3 - 2\pi \left(r_p - \frac{a}{2} \right)^2 \left(2r_p + \frac{a}{2} \right). \quad (7)$$

The porosity expression was then written as

$$\epsilon_a = 1 + \frac{4}{3}\pi + \frac{8}{3}\pi \left(\frac{r_p}{a} \right)^3 - 3\pi \left(\frac{r_p}{a} \right)^2 \quad (8)$$

(for $r_p > \frac{a}{2}$ which corresponds to $\epsilon_a < 0.476$).

Following a similar procedure as expressed by Eq. (4), flux expression was written and the tortuosity expression was obtained.

$$\begin{aligned} \frac{\epsilon_a}{\tau_a} = & \left[1 - \pi \left(\frac{r_p}{a} \right)^2 + 2 \left(\frac{r_p}{a} \right)^2 (\beta - \sin \beta) \right] + \left[\pi \frac{D_i}{D_{T_e}} \left(\frac{r_p}{a} \right)^2 \cos^2 \theta_1 \right] \\ & + \left[-2\pi \left(\frac{r_p}{a} \right)^2 X^* \times \left\{ \sin \frac{\beta}{2} - \frac{1}{2} \left(\frac{a}{r_p} \right) - X^* \ln \frac{\left(\sin \frac{\beta}{2} + X^* \right)}{\left(\frac{1}{2} \frac{a}{r_p} + X^* \right)} \right\} \right] \\ & + 4 \int_{1/2}^{r_p/a} \left(\frac{\pi}{2} - 2 \cos^{-1} \left(\frac{a}{2y} \right) \right) \left(\frac{1}{\frac{D_{T_e} X_2}{D_i} + 2 \frac{X_1}{a}} \right) \left(\frac{y}{a} \right) d \left(\frac{y}{a} \right) \end{aligned} \quad (9)$$

(for $\varepsilon_a < 0.476$), where

$$X^* = \frac{1}{2 \frac{r_p}{a} \left(\frac{D_{T_s}}{D_i} - 1 \right)} \quad (10)$$

$$\beta = 2 \cos^{-1} \left(\frac{1}{2} \frac{a}{r_p} \right) \quad (11)$$

and

$$\theta_1 = \sin^{-1} \left(\frac{1}{2} \frac{a}{r_p} \right) \quad (12)$$

In Eq. (9) the first square bracketed term corresponds to diffusion in macropores, second square bracket corresponds to micropore diffusion and the last term corresponds to the series contribution of macro and micropores. Our calculations have shown that if $\frac{D_{T_s}}{D_i} \geq 10^3$ only the first square bracketed term of Eq. (9) becomes significant and Eq. (9) becomes,

$$\frac{\varepsilon_a}{\tau_a} = 1 - \pi \left(\frac{r_p}{a} \right)^2 + 2 \left(\frac{r_p}{a} \right)^2 (\beta - \sin \beta). \quad (13)$$

For pellets with small macroporosities and with close average macro and micropore radii, micropore and series contributions also become significant.

Results

Predicted tortuosity factors from Eqs. (6) and (9) are plotted in Figure 2 as a function of macroporosity. For most of the predictions, knowledge about macroporosity is sufficient. Knowing macroporosity, corresponding $\left(\frac{r_p}{a} \right)$ ratio is estimated from Eq. (3) or (8), and then tortuosity is calculated from the corresponding equation (Eq. (6) or (9)). In Figure 2 predicted curve for $(D_{T_s}/D_i) \geq 10^3$ and for smaller D_{T_s}/D_i values are shown. As seen from this figure for smaller macroporosities and for smaller D_{T_s}/D_i values micro and series contributions also become significant. For bidispersed pellets of average macro and micropore radii ratio greater than 10^2 it is not necessary to have information about the value of D_{T_s}/D_i and the upper limit curve ($D_{T_s}/D_i \geq 10^3$) can be used. This upper limit curve can also be used for the prediction of tortuosity factors of pellets with monodispersed pore size distributions. Same analysis holds for such pellets by taking total porosity instead of macroporosity. We also recommend to use the total pore size distribution and total porosity for pellets with the ratio of average macro and micropore radii less than 10.

Many of the experimental tortuosity factors reported in the literature are also shown in Fig. 2. For bidisperse catalysts ε_a and for monobidispersed catalysts total porosities are used. As shown in the figure, predicted and experimental tortuosity values are in good agreement. Experimental values taken from the literature were obtained using different techniques. Also, the pore radius

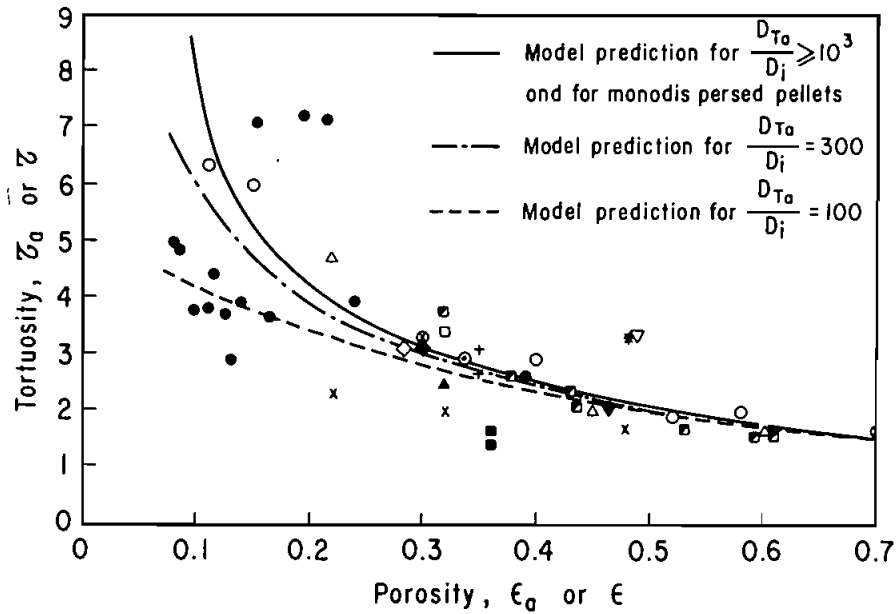


FIGURE 2 Predicted and experimental values of tortuosity

Symbol	Reference	Type of Porous Solid	ϵ_a or ϵ
•	Satterfield and Cadel (1968)	Commercial catalysts	ϵ_a, τ_a
○	This work	Alumina pellets with $\epsilon_i/(1 - \epsilon_a) = 0.49$	ϵ_a, τ_a
△	Kim and Smith (1974)	NiO pellets	ϵ, τ
□	Hashimoto and Smith (1973)	Molecular Sieve Pellets (5A)	ϵ_a, τ_a
■	Hashimoto and Smith (1974)	Boehmite pellets with $\epsilon_i/(1 - \epsilon_a) = 0.65$	ϵ_a, τ_a
×	Moffat (1978)	Quartz Pellet	ϵ, τ
+	Biswas <i>et al.</i> (1987)	γ -alumina pellet with $\epsilon_i/(1 - \epsilon_a) = 0.62$	ϵ_a, τ_a
▼	Villet and Wilhelm (1961)	Silica alumina catalyst	ϵ, τ
▲	Doğu and Ercan (1983)	Boehmite pellet with $\epsilon_i/(1 - \epsilon_a) = 0.62$	ϵ_a, τ_a
•	Doğu and Smith (1975)	Alumina pellet	ϵ_a, τ_a
▽	Schneider and Smith (1968)	Silica gel	ϵ, τ
⊙	Wakao and Smith (1962)	Boehmite pellet with $\epsilon_i/(1 - \epsilon_a) = 0.5$	ϵ_a, τ_a
⊕	Masamune and Smith (1962)	Ag pelletized powder $\epsilon_i/(1 - \epsilon_a) = 0.67$	ϵ_a, τ_a
◇	Weaver and Metzner (1966)	Porous Vycor	ϵ, τ
◆	Henry <i>et al.</i> (1967)	Porous Vycor	ϵ, τ
■	Weisz and Schwartz (1962)	Silica alumina and Chromia alumina beads	ϵ, τ

separating macro and micropores was chosen as different values by different researchers. Definition of macroporosity and selection of pore radius which separates macro and microporosities is very important for the correct prediction of τ_a from this model. It was interesting to note that experimental tortuosities for both, pellets with monodispersed and bidispersed pore size distributions gave

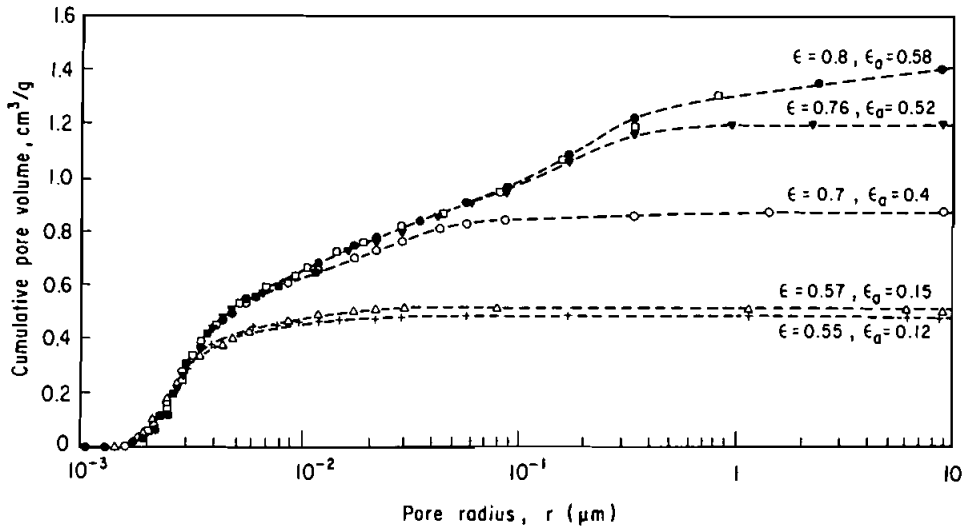


FIGURE 3 Pore size distributions of alumina pellets.

good agreement with the model predictions. Experimental values corresponding to pellets with macroporosities smaller than 0.08 were not included in Figure 2. Also, tortuosity values less than unity were not considered for this comparison. Such values are usually caused by the presence of surface diffusion or by the incorrect selection of average pore radius and porosity of the pores contributing to the diffusion flux.

In this work, effective diffusivities of alumina pellets of different porosities were also measured using the single pellet technique reported in the literature (Doğu and Smith, 1975, Doğu *et al.*, 1986). Tortuosity factor values were then determined from Eq. (1). In these calculations pores with radii greater than 35 Å were considered as macropores. As shown in Figure 3, up to 35 Å all the pore size distribution curves coincide. With this selection, $\epsilon_i/(1 - \epsilon_a)$ values were found to be essentially independent of compacting pressure and were equal to about 0.51. The experimental tortuosity values determined in this work showed good agreement with the predicted values (Figure 2).

In conclusion, the model proposed here allows quick prediction of tortuosity from Figure 2. It is a simple approach and the predicted values agree reasonably well with the experimental results.

NOMENCLATURE

a	Unit cell size (Figure 1)
a_0	Pore radius separating macro and micropores
C	Concentration
D_{AB}	Molecular diffusivity

D_e	Effective diffusivity
D_i	Effective micropore diffusivity
D_{K_A}	Knudsen diffusivity
D_T	Combined diffusivity defined by Eq. (2)
D_{T_m}	Combined diffusivity in the macropores
$f(r) dr$	Fraction of pores volume between pore radii r and $r + dr$
M_A	Molecular weight of A
N_e	Effective diffusion flux
r	Pore radius
r_p	Grain radius
X_1	Distance shown in Figure 1
X_2	Distance shown in Figure 1
y	Distance shown in Figure 1
y_A	Mole fraction of A

Greek Letters

α_i	$1 - (M_A/M_B)^{1/2}$
β	Angle shown in Figure 1b
ε	Total porosity
ε_a	Macro porosity
ε_i	Micro porosity
τ	Tortuosity factor based on total porosity
τ_a	Tortuosity factor based on macropores
θ	Angle shown in Figure 1a
θ_1	Angle shown in Figure 1b

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