A VARIATIONAL APPROACH TO A POROUS CATALYST

by

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The convection-diffusion process in porous electrodes depends greatly upon the porous structure. A fractal model for porous catalyst in a thin-zone bed reactor is established using He's fractal derivative, and a variational principle is also established in a fractal space, and an approximate solution is obtained. Additionally an ancient Chinese algorithm is adopted to solve an algebraic equation.

Key words: *porous medium, fractal variational principle, fractal calculus, approximate solution, nine chapters, ancient Chinese mathematics*

Introduction

Porous flows are widely used in engineering to enhance heat, mass and electron transfer, the porous structure or surface morphology can be used to control convection-diffusion process in porous electrodes [1, 2].

The continuum assumption, which is widely used in the fluid mechanics to establish governing equations, becomes invalid for a porous medium, so the traditional differential models cannot describe the porous effect on the flow properties. This paper suggests a fractal model for porous catalyst in a thin-zone bed reactor:

$$\frac{\mathrm{d}^2 M}{\mathrm{d}x^{2\alpha}} = k\left(1-\mathrm{e}^{-M}\right) \tag{1}$$

with initial conditions:

$$\frac{\mathrm{d}M}{\mathrm{d}x^{\alpha}}(0) = 0,\ \ M(0) = M_0 \tag{2}$$

where M is the dimensionless moment and k – the Damkohler number, the fractal derivative is defined [3-10]:

$$\frac{\mathrm{d}M}{\mathrm{d}x^{\alpha}}(x_0^{\alpha}) = \Gamma(1+\alpha) \lim_{\substack{x-x_0\to\Delta x \\ \Delta x\neq 0}} \frac{M(x^{\alpha})-M(x_0^{\alpha})}{(x-x_0)^{\alpha}} \tag{3}$$

$$\frac{\mathrm{d}^2 M}{\mathrm{d}x^{2\alpha}} = \frac{\mathrm{d}}{\mathrm{d}x^{\alpha}}\left(\frac{\mathrm{d}M}{\mathrm{d}x^{\alpha}}\right) \tag{4}$$

where α is the two-scale dimension, Δx – the smallest porosity, and porous size less than Δx is ignored.

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When $\alpha = 1$, eq. (1) becomes the traditional model for porous catalyst in a thin-zone bed reactor [1]:

$$\frac{\mathrm{d}^2 M}{\mathrm{d}x^2} = k\left(1 - \mathrm{e}^{-M}\right) \tag{5}$$

with initial conditions:

$$\frac{\mathrm{d}M}{\mathrm{d}x}(0) = 0, \ M(0) = M_0 \tag{6}$$

Variational principle

The variational principle for eq. (5) can be established by the semi-inverse method [11-15]:

$$J(M) = \int_0^1 \left\{ \frac{1}{2}\left(\frac{\mathrm{d}M}{\mathrm{d}x}\right)^2 + k\mathrm{e}^{-M} + kM \right\} \mathrm{d}x \tag{7}$$

Its stationary condition:

$$\frac{\partial L}{\partial M} - \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\partial L}{\partial M'}\right) = 0 \tag{8}$$

where $M' = \mathrm{d}M/\mathrm{d}x$, and L is the Lagrange function given:

$$L = \frac{1}{2}M'^2 + k\mathrm{e}^{-M} + kM \tag{9}$$

It is obvious:

$$\frac{\partial L}{\partial M} = -k\mathrm{e}^{-M} + k \tag{10}$$

$$\frac{\partial L}{\partial M'} = M' \tag{11}$$

Submitting eqs. (10) and (11) into eq. (8) results in the following Euler-Lagrange equation:

$$-k\mathrm{e}^{-M} + k - \frac{\mathrm{d}}{\mathrm{d}x}(M') = 0 \tag{12}$$

which is equivalent to eq. (5)

Similarly the variational principle for eq. (1):

$$J(M) = \int_{0^\alpha}^{1^\alpha} \left\{ \frac{1}{2}\left(\frac{\mathrm{d}M}{\mathrm{d}x^\alpha}\right)^2 + k\mathrm{e}^{-M} + kM \right\} \mathrm{d}x^\alpha \tag{13}$$

Its stationary condition:

$$\frac{\partial L}{\partial M} - \frac{\mathrm{d}}{\mathrm{d}x^\alpha}\left[\frac{\partial L}{\partial M^{(\alpha)}}\right] = 0 \tag{14}$$

where $M^{(\alpha)} = \mathrm{d}M/\mathrm{d}x^\alpha$, and L is the Lagrange function given:

$$L = \frac{1}{2}\left(\frac{\mathrm{d}M}{\mathrm{d}x^\alpha}\right)^2 + k\mathrm{e}^{-M} + kM \tag{15}$$

it is obvious:

$$\frac{\partial L}{\partial M} = -k\mathrm{e}^{-M} + k \tag{16}$$

$$\frac{\partial L}{\partial M^{(\alpha)}} = M^{(\alpha)} \tag{17}$$

Submitting eqs. (16) and (17) into eq. (14) results in the Euler-Lagrange equation:

$$-k\mathrm{e}^{-M} + k - \frac{\mathrm{d}}{\mathrm{d}x^{\alpha}}\left(\frac{\mathrm{d}M}{\mathrm{d}x^{\alpha}}\right) = 0 \tag{18}$$

which is equivalent to eq. (1).

Two-scale transform

The model by Constales *et al.* [1] ($\alpha = 1$) was derived by the continuum assumption, and it can be considered as an approximate model. To describe the effect of porous geometry on M, the porous structure must be considered, *e. g.*, we must model the process on a much smaller scale. In eq. (3), Δx is the smallest porous size. The two-scale transform [3-5]:

$$X = x^{\alpha} \tag{19}$$

Here x is the small scale to model porous effect, while X is the large-scale for the continuum assumption. The two-scale transform is to convert a fractal space on a small scale to a continuous space on a large-scale.

The variational formulation on the large-scale becomes:

$$J(M) = \int_0^1 \left\{\frac{1}{2}\left(\frac{\mathrm{d}M}{\mathrm{d}X}\right)^2 + k\mathrm{e}^{-M} + kM\right\}\mathrm{d}X \tag{20}$$

Its Euler-Lagrange equation:

$$\frac{\mathrm{d}^2 M}{\mathrm{d}X^2} = k\left(1 - \mathrm{e}^{-M}\right) \tag{21}$$

This is the traditional model derived by [1]:

We assume that the solution can be expressed:

$$M(X) = M_0 - a + aX^2 \tag{22}$$

Submitting eq. (22) into eq. (20), we obtain:

$$J(a) = \int_0^1 \left\{2a^2X^2 + k\exp(-M_0 + a - aX^2) + k(M_0 - a + aX^2)\right\}\mathrm{d}X \tag{23}$$

The stationary condition of eq. (23):

$$\frac{\mathrm{d}}{\mathrm{d}a}J(a) = \int_0^1 \left\{4aX^2 + k(1 - 2Xa)\exp(-M_0 + a - aX^2) + k(-1 + 2aX)\right\}\mathrm{d}X = 0 \tag{24}$$

From eq. (24) a can be solved by some a mathematical software. Here we use an ancient Chinese algorithm to solve a approximately [16, 17]. To illustrate the solution process, we consider the case of $k = 1$ and $M_0 = 1$. The ancient Chinese algorithm is to guess two arbitrary roots, saying $a_1 = 1/2$ and $a_2 = 1/3$, the residuals of eq. (24), respectively:

$$R_1 = \int_0^1 \left\{(1 - X)\exp(-0.5 - 0.5X^2) - 1 + X\right\}\mathrm{d}X = 0.447 \tag{25}$$

and

$$R_2 = \int_0^1 \left\{ \frac{4}{3}X^2 + \left(1 - \frac{2}{3}X\right)\exp\left(-1 + \frac{1}{3} - \frac{1}{3}X^2\right) - 1 + \frac{2}{3}X \right\} \mathrm{d}X = 0.094 \tag{26}$$

The ancient Chinese algorithm predicts an approximate value:

$$a = \frac{R_1 a_2 - R_2 a_1}{R_1 - R_2} = \frac{0.447 \times \frac{1}{3} - 0.094 \times \frac{1}{2}}{0.447 - 0.094} = 0.289 \tag{27}$$

We obtain an approximate solution:

$$M(X) = 0.711 + 0.289X^2 \tag{28}$$

Alternatively we can approximate e^{-M} in the form:

$$\mathrm{e}^{-M} \approx 1 - M + \frac{1}{2}M^2 \tag{29}$$

The variational formulation becomes:

$$J(M) = \int_0^1 \left\{ \frac{1}{2}\left(\frac{\mathrm{d}M}{\mathrm{d}X}\right)^2 + k\left(1 - M + \frac{1}{2}M^2\right) + kM \right\} \mathrm{d}X = \int_0^1 \left\{ \frac{1}{2}\left(\frac{\mathrm{d}M}{\mathrm{d}X}\right)^2 + k + \frac{1}{2}kM^2 \right\} \mathrm{d}X \tag{30}$$

In view of eq. (23), we have:

$$J(a) = \int_0^1 \left\{ 2a^2X^2 + k + \frac{1}{2}k\left(M_0 - a + aX^2\right)^2 \right\} \mathrm{d}X \tag{31}$$

Its stationary condition:

$$\frac{\mathrm{d}J}{\mathrm{d}a} = \int_0^1 \left\{ 4aX^2 + k(-1 + X^2)(M_0 - a + aX^2) \right\} dX = 0 \tag{32}$$

or

$$\frac{4}{3}a - \frac{2}{3}kM_0 + \frac{17}{15}a = 0 \tag{33}$$

We have:

$$a = 0.27027kM_0 \tag{34}$$

and

$$M(X) = M_0 - 0.27027kM_0 + 0.27027kM_0X^2 \tag{35}$$

Finally we obtain the approximate solution:

$$M(x) = M_0 - 0.27027kM_0 + 0.27027kM_0x^{2\alpha} \tag{36}$$

Discussion and conclusion

We can also use the fractal variational principle given in Eq. (13) to find an approximate solution. We assume:

$$M(x^\alpha) = M_0 - a + ax^{2\alpha} \tag{37}$$

Submitting eq. (37) into eq. (13), we obtain:

$$J(a)=\int_{0^\alpha}^{1^\alpha}\left\{2a^2x^{2\alpha}+k\exp(-M_0+a-ax^{2\alpha})+k(M_0-a+ax^{2\alpha})\right\}\mathrm{d}x^\alpha \tag{38}$$

The stationary condition of eq. (38):

$$\frac{\mathrm{d}}{\mathrm{d}a}J(a)=\int_{0^\alpha}^{1^\alpha}\left\{4ax^{2\alpha}+k(1-2x^\alpha a)\exp(-M_0+a-ax^{2\alpha})+k(-1+2ax^\alpha)\right\}\mathrm{d}x^\alpha=0 \tag{39}$$

From eq. (39), a can be determined in a similar way as previously discussed. To improve the accuracy, a higher order approximate solution can be assumed:

$$M(x)=M_0+\sum_{p=2}^{N}a_pX^p \tag{40}$$

It is obvious that Eq. (40) satisfies the initial conditions. Substituting Eq. (40) into Eq. (13), and setting:

$$\frac{\partial J}{\partial a_p}=0,\ \ (p=2\sim N) \tag{41}$$

we can solve a_p ($p = 2 \sim N$) from the previous algebra equations.

From eq. (36), we have:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}x}M(x)&=0.54054\alpha kM_0x^{2\alpha-1}\\ \frac{\mathrm{d}^2}{\mathrm{d}x^2}M(x)&=0.54054\alpha(2\alpha-1)kM_0x^{2\alpha-2}\\ \frac{\mathrm{d}^3}{\mathrm{d}x^3}M(x)&=0.54054\alpha(2\alpha-1)(2\alpha-2)kM_0x^{2\alpha-3}\end{aligned} \tag{42}$$

It is obvious:

$$\frac{\mathrm{d}}{\mathrm{d}x}M(0)=\frac{\mathrm{d}^2}{\mathrm{d}x^2}M(0)=\frac{\mathrm{d}^3}{\mathrm{d}x^3}M(0)=0\ \text{ for }\ \alpha>\frac{3}{2} \tag{43}$$

and

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}x}M(0)\to\infty\\ &\frac{\mathrm{d}^2}{\mathrm{d}x^2}M(0)\to\infty,\ \text{ for }\ \alpha<\frac{1}{2}\\ &\frac{\mathrm{d}^3}{\mathrm{d}x^3}M(0)\to\infty\end{aligned} \tag{44}$$

The properties given in eqs. (43) and (44) cannot be revealed by any continuum models. Similar phenomena were also observed in porous electrodes [18, 19].

To be concluded, this paper for the first time ever suggests a fractal model for porous catalyst using He's fractal derivative, the obtained solution shows that the order of the fractal derivative affects greatly the solution property, and it can be used to control the convection-diffusion process.

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