Analysis of the Process of Methane Pyrolysis in Polydisperse Porous Medium

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Abstract

The paper deals with the results of theoretical investigation of the process of methane pyrolysis in a polydisperse medium. A separate porous particle (macroparticle) is treated and this particle consists of different microparticles, which intersect randomly. A kinetic equation is used to describe the dynamics of a polydisperse system of microparticles in the process of methane pyrolysis. The reaction rate on the reaction surface of the particle is of the order of $n$ with respect to the gas reactant. The reactant is delivered to the porous macroparticle via external diffusion layer outside of the particle and internal diffusion layer in the particle pores. A generalization of the expression for porosity for a polydisperse medium is made. Comparison is made of the times required for filling the pores for different initial size distributions of particles. A general analytical expression is derived describing the dependence of variation of the inner reaction surface on the degree of metamorphism of the porous skeleton for an arbitrary initial size distribution of particles. Comparison is made of the dependences of the degree of metamorphism of porous skeleton on dimensionless time for different initial distributions, namely, monodisperse, uniform, and normally logarithmic with varying dispersion. It has been demonstrated that a polydisperse medium may be described by an effective structure parameter.

Introduction

The behavior of physicochemical processes in porous media is seriously affected by the geometric characteristics of the porous structure. Porous materials exhibit a complex irregular stochastic structure, which is manifested by the random pattern of local distribution of phases, local fields of concentrations, pressures, velocities, and so on. The process of chemical reaction in a polydisperse medium develops under conditions of diffusion and filtering transport of gases and liquids and is accompanied by phase transformations and by the phenomena of sintering and thermal deformation, which cause a variation in the structural characteristics of matter. These facts, along with the complex kinetic schemes of transformations and uncertainty of the values of kinetic constants, give rise to serious difficulties in developing mathematical models of reaction in porous media.

The theory of chemical reaction in stochastic systems presumes the development of probabilistic analysis of the interrelated domains of structure theory and heat- and mass transfer. Numerous studies are known at present dealing with both subjects. Heifetz and Neimark [1] treated in their monograph the main types of porous materials, their structural characteristics, and the respective mathematical models. They have briefly formulated the basic provisions of the thermodynamics of surface phenomena and outlined in detail the theories of motion of gas mixtures, convection and convective diffusion, multiphase filtering, and so on. Mozhaev [2, 3] presented the basic principles of the theory of dispersion turbulence and the basic theorems on the structure of chaotic homogeneous isotropic porous media.

The processes of combustion and gasification of porous media with due regard for the kinetics of chemical transformations are described, for example, in [4-11]. Aslanian and Maikov [4] took account of the polydispersity of the composition of the disperse
phase by way of splitting the entire spectrum of particles into separate fractions with subsequent calculation of the dynamics of each fraction. In order to allow for the polydispersity of coke during gasification, the probability density function of particle size distribution was used in [5,6]. A closed system of equations for the first and second moment was constructed. Simons and Finson [7,8] suggested a porous tree model. The equation describing the pore dynamics is similar to a kinetic equation. The realization of the models calls for the use of numerous fitting coefficients. Similar approaches to solving gasification problems are used in [9,10]. In order to allow for the polydispersity of solid fuel in combustion, Volkov et al. [11] used the probability density function of particle size distribution with the overall calculation of evolution of the entire system of particles.

Along with the processes of combustion and gasification (disintegration of the porous skeleton), the inverse processes (pore filling) such as methane pyrolysis during filtering through a porous medium are of great interest. The problem of methane pyrolysis was treated in [12-14] in view of the monodispersity of porous medium; the dependence of variation of the inner reaction surface on the degree of metamorphism of the porous skeleton for a monodisperse system of particles was obtained using the model of random spheres of [1].

This paper deals with the investigation of the process of methane pyrolysis in a porous medium in view of the polydispersity of porous material.

Structure Model

A separate porous particle (macroparticle) is treated. Let this particle consist of microparticles of radii \( r_1, r_2, ..., r_k \) and concentrations \( n_1, n_2, ..., n_k \), which intersect randomly, where \( k \) is the number of fractions. According to [1], the probability of an arbitrarily selected point to get into the pore space (a system of randomly intersecting particles of concentration \( n_i \) and radius \( r_i \)) is

\[
P_i = \left( 1 - \frac{n_i V_i}{n V} \right)^{n V}
\]  

(1)

From the condition of the absence of correlation in the distribution of centers of particles of all fractions, in view of Eq. (1), we derive that the sought probability is

\[
P = \prod_{i=1}^{k} \left( 1 - \frac{n_i V_i}{n V} \right)^{n V}
\]  

(2)

We go to the limit in expression (2) at \( nV \to \infty \) to derive the following expression for porosity:

\[
m = \exp \left( - \sum_{i=1}^{k} \frac{4}{3} \pi r^3 n_i \right)
\]  

(3)

Assume the size distribution of particles with the probability density function \( f(r) \). Then, expression (3) has the form

\[
m = \exp \left( - \int_{0}^{\infty} \frac{4}{3} \pi r^3 f(r) dr \right)
\]  

(4)

and the particle concentration is determined from the condition of normalization of the probability density function,

\[
n = \int_{0}^{\infty} f(r) dr
\]  

(5)

Equation (4) is a generalization of the expression for porosity [12] for a polydisperse medium.

Chemical Reaction

The rate of heterogeneous reaction on the reaction surface of a porous macroparticle depends on its temperature and on the concentration of the gas reactant on the surface.

The basic assumptions of the mathematical model of mass transfer in a porous particle may be formulated as follows.
1. The particle temperature is constant, and the thermal effect of the reaction is zero.
2. The reaction rate on the reaction surface of the particle is of the order of \( n \) with respect to the gas reactant and is defined by the expression

\[
q = \frac{dr}{dt} = \frac{k_r C_S^n}{\rho_c}
\]  

(6)

where \( k_r \) is the reaction rate constant in view of stoichiometry, \( C_S \) is the mass concentration of the reactant on the surface, and \( \rho_c \) is the density of the solid phase.
3. The reactant is delivered to the porous macroparticle via external diffusion layer outside of the particle and internal diffusion layer in the particle pores.

The flow of reactant via external diffusion layer
may be given by
\[ j_D = 4\pi R_p^2 k_D (C_0 - C_{in}) \]  
(7)

where \( C_0 \) is the bulk concentration of the gas component of the reaction outside of the macroparticle, \( C_{in} \) is the concentration of the gas component in the bulk of the particle, \( R_p \) is the macroparticle radius, and \( k_D \) is the coefficient of external mass transfer,
\[ k_D = \frac{\text{Nu} D}{2R_p} \]

Here, \( D \) is the diffusion coefficient of the gaseous reactant outside of the macroparticle, and \( \text{Nu} \) is the Nusselt number.

The flow of reactant via internal diffusion layer may be given by
\[ j_{in} = \frac{4\pi R_p^3 s D_{in}}{3} \left( \frac{\bar{N}_{in} - C_{in}}{r} \right) \]  
(8)

where \( D_{in} \) is the diffusion coefficient of the gaseous reactant in the macroparticle pores.

The rate of variation of the mass of reactant on the reaction surface will be written as
\[ j_S = \frac{4\pi R_p^3 s}{3} k C_S^n \]  
(9)

We can use the condition of equality of flows \( j_D = j_{in} = j_s \) and Eqs. (7), (8), and (9) to determine the concentration of gas component on the internal surface of the macroparticle by solving the transcendental equation
\[ C_S = C_0 \left( 1 + \frac{k C_S^{n-1} R_p s}{3 k_p} + \frac{k C_S^{n-1} r}{D_{in}} \right)^{-1} \]  
(10)

In view of Eq. (10), Eq. (6) for the first-order reaction may be written as
\[ q = \frac{k C_0 \mu_C}{\rho_C \mu_{C14}} \left( 1 + k_r + \frac{k R_p s}{3 k_p} \right)^{-1} \]  
(11)

or
\[ q = \eta (1 + k_e r + \psi)^{-1} \]  
(12)

where
\[ \eta = \frac{k C_0 \mu_C}{\rho_C \mu_{C14}}, \quad k_e = \frac{k}{D_{in}}, \quad \psi = \frac{k R_p s}{3 k_D} \]

Dynamic Equation for a Porous Structure

A kinetic equation of the form
\[ \frac{\partial f}{\partial t} + \frac{\partial (z_k f)}{\partial z_k} + F[f] = 0 \]  
(13)

is used to describe the dynamics of a polydisperse system of particles in the process of methane pyrolysis.

The probability density function (PDF) \( f(t, z_k) \) defines the probability density of the particle characteristic \( z_k \), and Eq. (13) describes the evolution of the polydisperse system of particles in the phase space \( z_k \). The first term of Eq. (13) denotes the time variation of the PDF, the second term, the variation of the PDF as a result of continuous processes at a rate \( \frac{\partial f}{\partial z_k} \), and the third term, jump-like variations of the PDF.

In calculating the processes of pyrolysis, we will take into account only the variation of the particle radius due to chemical reactions. In this case, the number of particles remains unvaried. Then, Eq. (13) in view of (6) will have the form
\[ \frac{\partial f}{\partial t} + \frac{\partial (q f)}{\partial r} = 0 \]  
(14)

We will multiply each term of the equation by the volume of one particle and perform integration over the entire spectrum of particle sizes. We will derive the equation
\[ \frac{\partial}{\partial t} \left( \int_0^\infty \frac{4\pi r^3 f dr}{3} \right) - \int_0^\infty 4\pi r^2 q f dr = 0 \]

In view of Eq. (4), we derive
\[ \frac{dm}{dt} = -< q > S > \]  
(15)

where
\[ < q > = \frac{\int_0^\infty q r^2 f(r,t) dr}{\int_0^\infty r^2 f(r,t) dr}, \quad < S > = \int_0^\infty m 4\pi r^2 f(r,t) dr = m \int_0^\infty 4\pi r^2 f(r,t) dr = m < S > \]

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We substitute the reaction rate in Eq. (15) by its mean value,
\[
\frac{\partial f}{\partial t} + \frac{\partial (\langle q > f)}{\partial r} = 0
\]
(16)

The validity of this substitution follows from the fact that the integration of Eq. (16) over the entire spectrum of particle sizes leads to the same balance equation (15).

Equation (16) has an analytical solution of the form
\[
f = f_0 \left( r - \int_0^t \langle q > dt \right)
\]
(17)
where \( f_0(r) \) is the initial radial distribution of particles.

Let \( \langle q > \) be independent of time; then, the solution of Eq. (17) has a simple physical meaning: the initial distribution moves along the r-axis at a rate \( \langle q > \) t is the quantity by which the initial particle radius increased by the moment of time t.

We will have the solution of Eq. (14), when the reaction rate of methane pyrolysis is described by Eq. (12).

We substitute Eq. (12) into (14) and perform differentiation to derive
\[
\frac{\partial f}{\partial t} + \frac{\partial f}{\partial r} \left( 1 + k_r + \psi \right) - \frac{\eta k_r f}{(1 + k_r + \psi)^2} = 0
\]
(18)

For the reaction rate in view of external diffusion resistance and reaction within a particle, the solution of Eq. (14) has the form
\[
f = \frac{r k_r + 1 + \psi}{\sqrt{(r k_r + 1 + \psi)^2 - 2\eta k_r t}} \times
\]
\[
\times \int_0^t \left( \frac{\sqrt{(r k_r + 1 + \psi)^2 - 2\eta k_r t}}{k_e} - \frac{1 + \psi}{k_e} \right) dt
\]
(19)
where \( \eta \) is the reduced rate constant, \( r k_e \) is the internal diffusion resistance, and \( \psi \) is the external diffusion resistance.

The solutions (17) and (19) describe the evolution of systems of particles which are subject to different initial size distributions of particles.

Results

We will treat the evolution of a system of particles subject to different initial distributions. Comparison must be performed for the same number densities \( n \) given by Eq. (6) and initial mass-average particle radii \( r_0 \),
\[
r_0 = \sqrt{\frac{\int_0^\infty 4\pi r^3 f(r)dr}{n}}
\]
(20)
and, as a consequence, for the same initial porosity given by Eq. (4).

**Monodisperse medium**

For a monodisperse medium, the initial distribution is preassigned as
\[
f_0 = n \delta(r - r_0).
\]
The solution (18) has the form
\[
f = n \delta \left( r - \frac{t}{\eta} < q > dt - r_0 \right)
\]
(21)
We will use the degree of metamorphism
\[
X = 1 - \frac{m}{m_0}
\]
and rewrite Eq. (15) as
\[
\frac{dX}{dt} = \langle q > \times (1 - X)
\]
(22)
We will treat the case of \( q = \eta \) i.e., a purely kinetic mode disregarding the external and internal diffusion resistance,
\[
< q >= \eta
\]
(23)
\[
< s > = n \int_0^\infty 4\pi r^2 \delta(r - \eta t - r_0)dr =
\]
\[
= 4\pi n (\eta t + r_0)^2 = \frac{3\phi}{r_0} (T + 1)^2
\]
(24)
where
\[
\phi = \frac{4}{3} \pi n r_0^3, \quad T = \frac{\eta t}{r_0}.
\]
The solution of Eq. (22) in view of (23) and (24) has the form
\[
X = 1 - \exp \left( -\phi(T + 3T^2 + 3T) \right)
\]
(25)

**Uniform distribution**

The uniform distribution is given by
\[ f_0 = n \frac{1}{b}, \quad 0 \leq r \leq b \]
\[ f_0 = 0, \quad b < r \]
where \( b \) is some constant. We will determine \( b \) from the condition (20),
\[ r_0^3 = \int_0^b \frac{r^3 \, dr}{b} = \frac{b^3}{4} \]

In accordance with Eqs. (23) and (24),
\[ < q > = \eta \]
\[ \phi(26) \]
\[ \phi(27) \]
\[ \phi(28) \]

**Logarithmically normal distribution**

The logarithmically normal distribution is given by
\[ f_0 = n \frac{1}{\sigma \sqrt{2\pi r}} \exp \left( -\frac{(\ln r - \ln < a >)^2}{2\sigma^2} \right) \]  (29)

where \( \ln < a > \) and \( \sigma^2 \) denote the mathematical expectation and dispersion of distribution.

The dispersion of a random quantity \( r \) distributed by logarithmically normal law is calculated by the formula [15]
\[ D = < a >^2 \exp(\sigma^2)(\exp(\sigma^2) - 1) \]  (30)

We can use condition (20) to derive
\[ r_0 = < a > \exp \left( \frac{3}{2} \sigma^2 \right) \]  (31)

In view of Eq. (31), the dispersion given by Eq. (30) is calculated by the formula
\[ D = r_0^2 \exp(-\sigma^2) \left[ 1 - \exp(-\sigma^2) \right] \]  (32)

One can see from Eq. (32) that, as the dispersion \( \sigma^2 \) of logarithmically normal distribution increases, the dispersion of distribution of the particle radius increases, passes through a maximum, and then decreases to zero. This is associated with the restriction imposed on the parameters of logarithmically normal distribution according to Eq. (30). The quantity \( r_0 \) is constant, and an increase in \( \sigma^2 \) causes a decrease in the parameter \( < a > \) whose logarithm is average for the distribution (29), and the distribution (29) tends to the delta function at the point \( r = 0 \), whose dispersion is zero.

According to Eqs. (23) and (24),
\[ < q > = \eta \]
\[ \phi(33) \]
\[ \phi(34) \]

The solution of Eq. (22) in view of (33) and (34) has the form
\[ X = 1 - \exp(-\phi(T^3 + 3T^2 \exp(-\sigma^2) + 3T \exp(-\sigma^2))) \]  (35)

Figure 1 gives the time dependence of pore filling for different initial distributions.

The differences are associated with the initial surface of particles: for monodisperse distribution according to Eq. (24),
\[ < s >_0 = \frac{3\phi}{r_0} \]  (36)

for uniform distribution according to Eq. (27),
\[ < s >_0 = \frac{4\sqrt{3} \phi}{r_0} \]  (37)

and for logarithmically normal distribution according to Eq. (34),
\[ < s >_0 = \frac{3\phi \exp(-\sigma^2)}{r_0} \]  (38)

According to Eq. (39), a monodisperse system has the maximum initial reaction area. The minimal time required for pore filling is observed in the case of monodisperse medium. One can see that, as the dispersion for logarithmically normal distribution decreases, the curves of pore filling (Fig. 1, curves 3-
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5) tend to the curve of monodisperse distribution (curve 1).

Fig. 1. The degree of metamorphism of porous skeleton as a function of dimensionless time for different initial distributions: 1, monodisperse; 2, uniform; 3-5, normal logarithmic with dispersion of 0.3, 1, and 2, respectively. Calculations were performed by formulas (25), (28), (35).

Arbitrary initial distribution

We will derive relations for determining the degree of metamorphism for an arbitrary initial size distribution of particles. According to expression (15) in view of solution (17), the total internal surface is determined by the formula

\[ <S> = \int_{0}^{\infty} 4\pi r^2 f_0(r) \left( r - \int_{0}^{q} \frac{dr}{<q^2>dt} \right) \, dr \]  \hspace{2cm} (39)

One can perform the substitution of variables

\[ \xi = r - \int_{0}^{q} \frac{dr}{<q^2>dt} \] and, in view of Eq. (23), write Eq. (39) as

\[ <S> = m \int_{0}^{\infty} 4\pi (\xi + \eta t)^2 f_0(\xi) d\xi = m4\pi \left( \int_{0}^{\infty} \xi^2 f_0(\xi) d\xi + 2\eta t \int_{0}^{\infty} \xi f_0(\xi) d\xi + (\eta t)^2 \int_{0}^{\infty} f_0(\xi) d\xi \right) = m4\pi m(D + A^2) + 2\eta A + (\eta t)^2 \] \hspace{2cm} (40)

The resultant integrals are, by definition, the second, first, and zero distribution moments [15], D and A are the distribution parameters.

The solution of Eq. (22) in view of (40) has the form

\[ X = 1 - \exp \left( -\varphi \left( 3T \frac{D}{r_0^2} + \left( \frac{T + A}{r_0} \right) ^3 - \left( \frac{A}{r_0} \right) ^3 \right) \right) \]  \hspace{2cm} (41)

Equation (42) represents a general solution with an arbitrary initial radial distribution of particles. The equation involves parameters defining the distribution (mean and dispersion) and the parameter \( r_0 \) (mass average radius) which is calculated directly by the given distribution at the initial moment of time. Equation (20) gives the correlation between the distribution parameters and the mass average radius.

The relative reaction surface as a function of the degree of metamorphism of porous skeleton

We will derive an equation relating the relative internal reaction surface of a macroparticle to the degree of metamorphism of porous skeleton. According to Eq. (15),

\[ \frac{d <S>}{dt} = <s> \frac{dm}{dt} + m \frac{d<s>}{dt} \] \hspace{2cm} (42)

One can use the dimensionless variable \( F = s/s_0 \) (relative internal surface) and reduce the set of equations (22) and (42) to the differential equation

\[ \frac{dF}{dX} = \frac{2}{3} F \frac{r_0 \theta}{\sqrt{D + A^2}} x \times \sqrt{\frac{D}{D + A^2}} \times \frac{F}{1 - X} \times \frac{D}{1 - X} = \frac{F}{1 - X} \] \hspace{2cm} (43)
where \( \theta_0 = \frac{3m_0}{r_0s_0} \) is the dimensionless structure parameter. The physical meaning of the structure parameter is explained in Fig. 2. It is the measure of deviation from regular packing.

Equation (43) has the analytical solution

\[
\left( F - \frac{D}{D + A^2} (1 - X) \right)^{1/2} \left( F + \frac{2D}{D + A^2} (1 - X) \right) = \left( 1 - X \right)^{1/2} \left( \frac{a}{\sqrt{D + A^2}} \left( 1 + \frac{2D}{D + A^2} \right) - \theta_{\text{eff}} \ln(1 - X) \right)
\] (44)

where

\[
\theta_{\text{eff}} = \frac{r_0}{\sqrt{D + A^2}} \theta_0
\] (45)

In Eq. (45), \( \theta_{\text{eff}} \) is the effective structure parameter for an arbitrary polydisperse distribution of particles. This parameter includes the distribution parameters \( r_0, D, \) and \( A \), determined by Eqs. (20) and (40); \( \theta_0 \) is the dimensionless structure parameter defined above. Expression (45) defines the deviation of the structure parameter for polydisperse medium from that for monodisperse medium with the parameter \( \theta_0 \).

Equation (44) is a generalization of the solution for a monodisperse medium, obtained in [12], to the case of an arbitrary polydisperse medium.

Figure 3 gives the dependence of the relative internal reaction surface of a macroparticle on the degree of metamorphism of porous skeleton for different initial distributions. We observe qualitative agreement in the behavior of three distributions exhibiting minor dispersion (curves 1-3). The effective structure parameter according to formula (45) is \( \theta_{\text{eff}} = \theta_0 = 1 \) for monodisperse distribution and \( \theta_{\text{eff}} = 1.09 \) for uniform distribution; for logarithmically normal distribution it is \( \sigma^2 = 0.3 \) and \( \theta_{\text{eff}} = 1.16; \sigma^2 = 1, \) and \( \theta_{\text{eff}} = 1.64; \sigma^2 = 2 \) and \( \theta_{\text{eff}} = 2.71 \).

It follows from Eq. (45) that the minimal value of the structure parameter is equal to \( \theta_0 \) for a monodisperse medium. Any other medium (polydisperse) is described by a parameter exceeding \( \theta_0 \). Figure 4 gives distributions at \( \theta_0 = 1 \). The difference between the
times of the process (see Fig. 3) may further be attributed to the fact that the medium structure in the case of polydisperse medium is looser (see Fig. 2, case of $\theta_0 > 1$) and, therefore, a longer time is required for pore filling.

Figure 4 gives the dependence of the relative internal reaction surface of a macroparticle on dimensionless time for different initial distributions. The distributions with $\theta_{\text{eff}} = \theta_0 = 1$ have the maximal initial surface. During the process of pyrolysis, the pore filling begins, and the surface monotonically decreases. The distributions with $\theta_{\text{eff}} > \theta_0 = 1$ need time to reach the maximal surface; accordingly, this affects the time required for filling the pores.

Figures 5 and 6 give the dependence of the degree of metamorphism of porous skeleton on dimensionless time and the dependence of the relative internal reaction surface of a macroparticle on the degree of metamorphism of porous skeleton, respectively, for different initial distributions at $\theta_0 = 5$. The
Similar regularities are obtained when the solution (19) is used; however, they are more cumbersome and, in some cases, require the use of numerical methods for solving equations.

**Conclusions**

A general expression has been derived, for the dependence of the variation of the internal reaction surface on the degree of metamorphism of porous skeleton for an arbitrary initial size distribution of particles, with a generalization of the model of random spheres for a polydisperse medium.

Comparison has been made of the dependences of the degree of metamorphism of porous skeleton on dimensionless time for different initial distributions, namely, monodisperse, uniform, and normally logarithmic with varying dispersion. The minimal time required for pore filling is observed in the case of a monodisperse medium.

It has been demonstrated that a polydisperse medium may be described by an effective structure parameter whose magnitude always exceeds that of the similar parameter for a monodisperse medium; this corresponds to a looser structure and smaller initial reaction surface.

The suggested approach based on the solution of the kinetic equation for the probability density function may be used in solving similar problems of chemical kinetics in an evolving porous medium.

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