Mathematical model of Fischer-Tropsch catalyst pellet with pointed centers of synthesis

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Abstract. The productivity of Fischer-Tropsch reactors is determined by the efficiency of heat and mass transfer processes inside the catalyst pellets. To reduce the diffusion resistance, the pellet base is made porous. The porous structure of the granules causes a discrete arrangement of cobalt metallic microparticles whose size can reach tens of microns. The distance between these active centres significantly exceeds their characteristic size and the homogeneous catalyst model is incorrect. A mathematical model of heat and mass transfer processes inside a porous spherical pellet with localised active centres is proposed. The heat of the exothermic synthesis reaction is removed from the surface of the granule to the synthesis gas stream washing the catalyst pellet by heat transfer. The components of the synthesis gas enter the granule surface as a result of mass transfer. On the basis of the self-consistent field method, the values of the temperature and concentration of the synthesis gas components at the active centres were determined. It is shown that there is a critical temperature of the synthesis gas washing the granule, exceeding critical temperature leads to a substantial overheating of the active centres. In this case, the surface of the catalyst pellet is superheated slightly. The principal difference between the homogeneous and heterogeneous models in catalytic reactions is discussed.

1. Introduction

Heterogeneous chemical reactions are widely used in power engineering and chemical industries. For example, coal burning at thermal power plants, gasification of coal, gasification of shale and household waste, cleaning exhaust gases from sulfur oxides in absorbers, catalytic synthesis reactors. In these industrial applications heterogeneous reactions occurs inside the porous granules. We can distinguish two types of chemically active inner porous surface. In the first type, the absorption of active components from the gas phase occurs at any point in the porous volume of the pellet, for example, combustion of coke, gasification of coal, absorption of sulfur oxides. In this case, a homogeneous approximation can be used to describe the reactions in the volume of the granules. A wide range of models designed for homogeneous reactions: shrinking core model, models taking into account the dynamics of change the pore structure, percolation and fractal models [1–16].

The second type with discrete location reaction active sites, generally include catalysts granules. In this paper, the catalyst for the synthesis of artificial oil on the base of Fischer-Tropsch technology is considered. Fischer-Tropsch synthesis is a promising way of utilization of petroleum gas, processing of gaseous products gasification of coal and organic waste. Industrial synthesis reactor is collected from the reactor tubes, which are arranged inside millimeters catalyst pellets. Synthesis gas consisting of a mixture of hydrogen and carbon monoxide is pumped through fixed bed of catalytic granules. As a result, inside the reactor tube formed of gaseous and liquid products. Synthesis of heavy
hydrocarbons is accompanied by the release of a significant amount of heat. The synthesis products and safety of the reactor is determined by the processes of heat and mass transfer inside the catalyst pellet. Synthesis reactions take place on cobalt microparticles. Modern promising catalysts are highly porous structure, in which are embedded metal particles of cobalt with diameter of order of ten microns. The distance between the microparticles is much greater than their diameter [17–29]. In this case, the use of a homogeneous model for describing heat and mass transfer processes inside a catalytic particle is not correct.

The main goal of the paper is to propose a technique for calculating the temperature and synthesis gas concentration at local reaction centers and to estimate the temperature from which the Fischer-Tropsch catalyst granule loses the thermal stability.

Exothermic synthesis reactions lead to overheating of the active sites as compared with the temperature of the reactor tube. High temperature synthesis centers degrade the product composition and increases the power of heat release. Uncontrolled heat release can cause an accident with serious consequences. Thermocouples in the reactor tube show the surface temperature of the catalyst pellets. The measured temperature can be significantly lower than the actual temperature of the local active centers inside the granule. Development of a mathematical model of processes of heat and mass transfer within the porous catalyst pellets with discrete local centers of reaction is an important task.

It should be noted the fundamental complexity of the problem considered in this paper. In a homogeneous approximation, the calculation of temperature and concentration inside the granule is carried out on the basis of well-proven numerical iterative solutions for a system of nonstationary heat conduction and diffusion equations with sources and sinks uniformly distributed in the bulk of the granule. In the case of discrete reaction centers, the calculation techniques are developed to a much lesser degree. The complexity of the problem under study lies in the fact that the temperature and the concentrations of the absorbed gases at the active reaction centers are unknown. The temperature and concentration of synthesis gas on the localized active center depend on the boundary conditions of the granule and the collective thermal and concentration influence of all other centers. In our work, we first proposed a model for calculating the steady-state temperature of a catalyst pellet with local reaction centers. The calculation of the temperature of active reaction centers is based on the idea of a self-consistent field. First, we assume that the heat release power of the reaction centers is known. On the basis of the analytical solution describing the distribution of temperature inside the granule, we calculate the average temperature of the reaction centers, which we then substitute into the heat release formula. The system of transcendental algebraic equations is transformed to a system of ordinary differential equations of relaxation type and solved numerically until a stationary solution is reached.

Comparison with the results of calculations by the homogeneous model in which synthesis proceeds anywhere catalyst volume illustrates a fundamental difference from the pattern with discrete reaction centers. Note that homogeneous description cannot explain the recently discovered phenomenon of temperature hysteresis in heterogeneous catalysis.

2. Basic equations

We study the catalyst pellet of Fischer–Tropsch technology for synthesis the liquid high molecular hydrocarbons [30]. Synthesis of hydrocarbons occurs as a result of the formation on cobalt the intermediate microparticles (−CH₂−), which propagate the chain of transformation

\[ 2nH_2 + nCO \rightarrow (\text{−CH}_2\text{−})_n + nH_2O \]  \hspace{1cm} (1)

The major part of organic compounds formed on cobalt is paraffins. The molecular weight distribution of the products of synthesis is regulated by the chain propagation constant \( \alpha_{\text{FT}} \) and is described by the Schulz-Flory distribution.

Inside the spherical porous catalyst pellets with a diameter \( d_p \) there are placed microparticles of metallic cobalt with a diameter \( d_{\text{Co}} \). The diameter of the granule significantly exceeds the diameter of
the microparticles $d_{gr} \gg d_{co}$, therefore we model cobalt microparticles as a mathematical point. The equation for the temperature of a granule $T_{gr}$ with point sources of heat arbitrarily located inside the granule has the form

$$\rho_{gr} c_{gr} \frac{\partial T_{gr}}{\partial t} = \lambda_{gr} \Delta T_{gr} + \sum_{i=1}^{N_0} Q_{FT i} m_{co} \Phi_{co} \left(T_0^{(i)}, P_{CO}^{(i)}, P_{H_2}^{(i)}\right) \delta(r - r_0^{(i)})$$

(2)

Here $\rho_{gr}, c_{gr}, \lambda_{gr}$ are density, heat capacity and heat conduction of the pellet material; $Q_{FT i}$ is the heat of exothermic synthesis reaction; $m_{co}$ mass of cobalt in the granule; $r_0^{(i)}$ are radius vectors of active centres; $T_0^{(i)}, P_{CO}^{(i)}, P_{H_2}^{(i)}$ are temperature, pressure of carbon monoxide and hydrogen at the active centres; $\Phi_{co} \left(T, P_{CO}, P_{H_2}\right)$ is semiempirical function describing the rate of consumption of carbon monoxide; $N_0$ is number of active centres in the granule; $\delta(r) = \delta(x) \delta(y) \delta(z)$ is Dirac delta-function.

Dirac delta-function is normalized as

$$\int \delta(r) \, dr = 1$$

Here $dr = dx \, dy \, dz$ is differential of the volume.

The boundary condition for the temperature on the surface of the granule has the form

$$-\lambda_{gr} \frac{\partial T_{gr}}{\partial r} \bigg|_{r=d_{gr}/2} = \alpha_0 \left(T_{gr} \bigg|_{r=d_{gr}/2} - T_\infty\right)$$

(3)

Here $\alpha_0$ is heat transfer coefficient.

The equation for the concentration of carbon monoxide $C_{CO}$ is written as

$$\frac{\partial C_{CO}}{\partial t} = D_{co} \Delta C_{CO} - \sum_{i=1}^{N_0} m_{co} \Phi_{CO} \left(T_0^{(i)}, P_{CO}^{(i)}, P_{H_2}^{(i)}\right) \delta(r - r_0^{(i)})$$

(4)

Here $D_{co}$ is diffusion coefficient of carbon monoxide inside the porous granule.

The boundary condition describes the mass exchange by carbon monoxide through the granule surface

$$-D_{co} \frac{\partial C_{CO}}{\partial r} \bigg|_{r=d_{gr}/2} = \beta_{CO} \left(C_{CO} \bigg|_{r=d_{gr}/2} - C_{CO}^\infty\right)$$

(5)

Here $C_{CO}^\infty$ is concentration of carbon monoxide outside the granule; $\beta_{CO}$ is mass transfer coefficient for CO.

In a similar way, we write down the equation of balance of hydrogen concentration inside the granule

$$\frac{\partial C_{H_2}}{\partial t} = D_{H_2} \Delta C_{H_2} - \zeta_{H_2,CO} \sum_{i=1}^{N_0} m_{co} \Phi_{CO} \left(T_0^{(i)}, P_{CO}^{(i)}, P_{H_2}^{(i)}\right) \delta(r - r_0^{(i)})$$

(6)
Here \( D_{H_2} \) is diffusion coefficient of hydrogen; \( \zeta_{H_2/CO} \) is stoichiometric coefficient from equation (1).

On the boundary of the granule we set the boundary condition for mass transfer

\[
-D_{H_2} \frac{\partial C_{H_2}}{\partial r} \bigg|_{r=d_g/2} = \beta_{H_2} \left( C_{H_2}^{\infty} - C_{H_2}^r \right)
\]

(7)

Here \( \beta_{H_2} \) is mass transfer coefficient \( H_2 \); \( C_{H_2}^{\infty} \) is hydrogen concentration outside the granule.

3. Equations in dimensionless form

We proceed in the equations of heat balance (2) and concentrations (4), (6) to dimensionless form. The dimensionless temperature and the concentrations of CO and \( H_2 \) are determined, respectively, as

\[
\Theta = \frac{T_g - T_\infty}{T_\infty}, \quad \Psi_{CO} = \frac{C_{CO}^{\infty} - C_{CO}}{C_{CO}^{\infty}}, \quad \Psi_{H_2} = \frac{C_{H_2}^{\infty} - C_{H_2}}{C_{H_2}^{\infty}}
\]

The general form of the function describing the rate of consumption of carbon monoxide on cobalt is

\[
\Phi_{CO} (T_g, P_{CO}, P_{H_2}) = a_0^* \exp \left( E_a^* - \frac{\Theta}{1+\Theta} \right) \left\{ 1 + b_0^* \exp \left( E_a^* - \frac{\Theta}{1+\Theta} \right) \right\}^2
\]

(8)

Here \( E_a^* = E_a / R_0 T_\infty \), \( E_o^* = E_o / R_0 T_\infty \) are dimensionless activation energies; \( a_0^* = a_0 (P_{CO}, P_{H_2}) \exp (-E_a^*) \), \( b_0^* = b_0 (P_{CO}, P_{H_2}) \exp (-E_o^*) \) are empirical function; \( R_0 \) is universal gas constant.

The time scale is defined as the characteristic heat diffusion time inside the granule

\[
t_0 = \left( \frac{d_g/2}{\kappa_g} \right)^2, \quad \kappa_g = \kappa_g, \quad \lambda_g = \kappa_g / (\rho_g c_g)
\]

is thermal diffusivity of the granule. The dimensionless time in this case is \( \xi = t / t_0 = \frac{\kappa_g}{d_g/2} \). As the spatial scale, we select the radius of the granule, then the dimensionless coordinate is equal to \( \eta = 2r / d_g \).

The equation for the dimensionless temperature of the granule (2) with point sources of the reaction takes the form

\[
\frac{\partial \Theta}{\partial \xi} = \Delta \Theta + 4\pi \sum_{i=1}^{N_r} \Xi_{i}^{(i)} \delta (\eta - \eta_{i}^{(i)})
\]

(9)

Here \( \eta_{i}^{(i)} = 2r_{i}^{(i)}/d_g \) are dimensionless radius vectors of local centers of reaction; \( \Xi_{i}^{(i)} \) is dimensionless heat release during synthesis reactions

\[
4\pi \Xi_{i}^{(i)} = \Omega_{i}^{(i)} \exp \left[ \frac{E_a^* \Theta_0^{(i)}/(1+\Theta_0^{(i)})}{1 + b_0^* \exp \left( E_o^* \Theta_0^{(i)}/(1+\Theta_0^{(i)}) \right)} \right], \quad \Omega_{i}^{(i)} = \frac{Q_{i}^{(i)} m_{CO} \rho_0 (R_{i}^{(i)}, P_{i}^{(i)}) \exp (-E_o^*)}{\lambda_g T_s (d_g/2)}
\]
Here $\Theta^{(i)}_0 = \Theta\left(\eta^{(i)}_0\right)$ are the dimensionless temperatures of the active reaction centers.

The boundary condition (4) in the dimensionless form is rewritten as

$$\left.\frac{\partial \Theta}{\partial \eta} + \alpha^*_0 \Theta\right|_{\eta^{(i)}} = 0 \quad (10)$$

Here is $\alpha^*_0 = \alpha_0 \left(d_p/2\right)/\lambda_{\text{gr}}$ is dimensionless coefficient of heat transfer.

Equations for the dimensionless concentrations of CO (4) and H2 (6) take the form

$$\text{Le}_{CO} \frac{\partial \psi_{CO}}{\partial \xi} = \Delta \psi_{CO} + 4\pi \sum_{i=1}^{N_0} \Xi^{(i)}_{CO} \delta\left(\eta - \eta^{(i)}_0\right)$$

$$\text{Le}_{H_2} \frac{\partial \psi_{H_2}}{\partial \xi} = \Delta \psi_{H_2} + 4\pi \sum_{i=1}^{N_0} \Xi^{(i)}_{H_2} \delta\left(\eta - \eta^{(i)}_0\right)$$

Here $\text{Le}_{CO} = \chi_{CO}/D_{CO}$, $\text{Le}_{H_2} = \chi_{H_2}/D_{H_2}$ are Lewis numbers of CO and H2.

The dimensionless rates of consumption of carbon monoxide and hydrogen are equal

$$4\pi \Xi^{(i)}_{CO} = \Omega^{(i)}_{CO} \frac{\exp\left[E_a^*_i \Theta^{(i)}_0 \left(1 + \Theta^{(i)}_0\right)\right]}{\left(1 + b^*_i \exp\left[E_a^*_i \Theta^{(i)}_0 \left(1 + \Theta^{(i)}_0\right)\right]\right]^2} \cdot \Omega^{(i)}_{CO} = \frac{m_{CO} a_0 \left(P_{CO}^{(i)} \cdot P_{H_2}^{(i)}\right) \exp\left(-E_a^*_i\right)}{D_{CO} C_{CO} \left(d_p/2\right)} \quad (11)$$

$$4\pi \Xi^{(i)}_{H_2} = \Omega^{(i)}_{H_2} \frac{\exp\left[E_a^*_i \Theta^{(i)}_0 \left(1 + \Theta^{(i)}_0\right)\right]}{\left(1 + b^*_i \exp\left[E_a^*_i \Theta^{(i)}_0 \left(1 + \Theta^{(i)}_0\right)\right]\right]^2} \cdot \Omega^{(i)}_{H_2} = \frac{m_{CO} a_0 \left(P_{CO}^{(i)} \cdot P_{H_2}^{(i)}\right) \exp\left(-E_a^*_i\right)}{D_{H_2} C_{H_2} \left(d_p/2\right)} \quad (12)$$

The boundary conditions for the balance equations for the concentrations of CO (5) and H2 (7) in the dimensionless form are rewritten as

$$\left.\frac{\partial \psi_{CO}}{\partial \eta} + \beta^*_{CO} \psi_{CO}\right|_{\eta^{(i)}} = 0 \quad , \quad \beta^*_{CO} = \frac{\beta_{CO} \left(d_p/2\right)}{D_{CO}}$$

$$\left.\frac{\partial \psi_{H_2}}{\partial \eta} + \beta^*_{H_2} \psi_{H_2}\right|_{\eta^{(i)}} = 0 \quad , \quad \beta^*_{H_2} = \frac{\beta_{H_2} \left(d_p/2\right)}{D_{H_2}}$$

Here $\beta^*_{CO}$, $\beta^*_{H_2}$ are dimensionless coefficients of mass transfer.

4. Stationary distribution of temperature and synthesis gas in the granule

We illustrate the method of self-consistent calculation of the temperature and the concentration distributions inside the granule on the example of the temperature equation.

In the stationary case, the equation for the temperature (8) has the form
\[
\Delta \Theta + 4\pi \sum_{i=1}^{N_i} \varepsilon^{(i)}(\eta - \eta_0^{(i)}) = 0
\]  

(13)

The boundary condition for equation (13) coincides with equation (10). We are looking for a solution of the problem in a spherical coordinate system (see figure 1).

![Figure 1. Coordinate system with one active centre.](image)

For simplicity considerations we first assume that chemical reaction rate is independent of the concentration CO and H\textsubscript{2}, in formulas (11) and (12) \( a_i^0, b_i^0 = \text{const} \). Initially, we suppose that heat power in the equation (13) is given. The distribution of temperature inside the granule is the sum of the temperature distributions from each heat source

\[
\Theta(\eta) = \sum_{i=1}^{N_i} \Theta^{(i)}(\eta, \eta_0^{(i)})
\]

(14)

Here \( \Theta^{(i)}(\eta, \eta_0^{(i)}) \) is the temperature distribution at a point with a radius vector \( \eta \) from a source located at a point with a radius vector \( \eta_0^{(i)} \).

The temperature distribution generated by a source located at the point \( \eta_0^{(i)} \) we found as the solution of the following problem

\[
\Delta \Theta^{(i)} + 4\pi \varepsilon^{(i)}(\eta - \eta_0^{(i)}) = 0 , \quad \left( \frac{\partial \Theta^{(i)}}{\partial \eta} + a_i^0 \Theta^{(i)} \right)_{\eta^{(i)}} = 0
\]

(15)

The solution of the problem (15) is the sum of two components

\[
\Theta^{(i)}(\eta, \eta_0^{(i)}) = \Theta_1^{(i)}(\eta, \eta_0^{(i)}) + \Theta_2^{(i)}(\eta, \eta_0^{(i)})
\]

(16)

The first summand in the sum (16) \( \Theta_1^{(i)}(\eta, \eta_0^{(i)}) \) is the solution of the inhomogeneous equation in an infinite space with a point source.
\[
\Theta^{(i)}(\eta_0^{(i)}) = \frac{\Xi^{(i)}(\eta_0^{(i)})}{|\eta - \eta_0^{(i)}|} = \frac{\Xi^{(i)}(\eta_0^{(i)})}{\sqrt{\eta^2 - 2\eta_0^{(i)} \cos(\Delta \theta_0^{(i)}) + (\eta_0^{(i)})^2}}
\]

(17)

Where the cosine of the angle \( \Delta \theta_0^{(i)} \) between the two vectors in the spherical coordinate system \( \eta = \{\eta_1, \eta_2, \eta_3, \eta_4\} \) and \( \eta_0^{(i)} = \{\eta_0^{(i)}_1, \eta_0^{(i)}_2, \eta_0^{(i)}_3, \eta_0^{(i)}_4\} \) (see figure 1) is calculated by the formula

\[
\cos(\Delta \theta_0^{(i)}) = \cos \theta \cos \theta_0^{(i)} + \sin \theta \sin \theta_0^{(i)} \cos(\phi - \phi_0^{(i)})
\]

The second term in the sum (16) is a solution of the Laplace equation

\[
\Delta \Theta^{(i)}(\eta | \eta_0^{(i)}) = 0
\]

In the spherical coordinate system, the general formula for the solution of the Laplace equation for the internal problem has the form [31]

\[
\Theta^{(i)}(\eta_0^{(i)}) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \eta^m \left[ A^{(i)}_{m,n} \cos(m \varphi) + B^{(i)}_{m,n} \sin(m \varphi) \right] P^m_n(\cos \theta)
\]

Here \( P^m_n(x) \) are associated Legendre polynomials.

Coefficients \( A^{(i)}_{m,n}, B^{(i)}_{m,n} \) are determined from the boundary conditions of the problem (15). For this purpose we expand the solution of the inhomogeneous equation (17) into a series of associated Legendre polynomials [31]

\[
\Theta^{(i)}(\eta | \eta_0^{(i)}) = \Xi^{(i)} \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \varepsilon_m \frac{(n-m)!}{(n+m)!} \cos \left[ m(\phi - \phi_0^{(i)}) \right] P^m_n(\cos \theta) P^m_n(\cos \theta_0^{(i)})
\]

\[\times\left\{\begin{array}{l}
\frac{\eta^n}{\eta_0^{(i)}}^{n+1}, \quad \eta \leq \eta_0^{(i)} \\
\frac{\eta_0^{(i)}}{\eta}^{n}, \quad \eta \geq \eta_0^{(i)}
\end{array}\right\}
\]

Where the multiplier is defined as \( \varepsilon_m = \left\{\begin{array}{l}
1, \quad m = 0 \\
2, \quad m \neq 0
\end{array}\right\} \).

Near the surface of the granule \( \eta \geq \max \{\eta_0^{(i)}\} \), we write the expansion of the general solution (16) in a series in the Legendre polynomials

\[
\Theta^{(i)}(\eta) = \Xi^{(i)} \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{(n-m)!}{(n+m)!} \cos \left[ m(\phi - \phi_0^{(i)}) \right] P^m_n(\cos \theta) P^m_n(\cos \theta_0^{(i)}) \frac{(\eta_0^{(i)})^n}{\eta^{n+1}}
\]

\[+\sum_{n=0}^{\infty} \sum_{m=-n}^{n} \eta^n \left[ A^{(i)}_{m,n} \cos(m \varphi) + B^{(i)}_{m,n} \sin(m \varphi) \right] P^m_n(\cos \theta)
\]
We substitute this expansion into the boundary conditions (15) and use the orthogonality condition associated Legendre polynomials. As a result, we find the expression for the unknown coefficients

\[ A^{(i)}_{m,n} = \sum_{l} C^{(l)}_{m,n} \frac{(n-m)!}{(n+m)!} \cos(m\varphi_{i}) P_{n}^{(m)}(\cos \theta_{i}) \left( \eta_{0i}^{(m)} \right)^{n} \frac{(n+1)-\alpha_{0i}}{n+\alpha_{0i}} \]

\[ B^{(i)}_{m,n} = \sum_{l} C^{(l)}_{m,n} \frac{(n-m)!}{(n+m)!} \sin(m\varphi_{i}) P_{n}^{(m)}(\cos \theta_{i}) \left( \eta_{0i}^{(m)} \right)^{n} \frac{(n+1)-\alpha_{0i}}{n+\alpha_{0i}} \]

Considering the obtained expressions for the coefficients \( A^{(i)}_{m,n} \), \( B^{(i)}_{m,n} \) the solution (16) is rewritten in a compact form

\[ \Theta^{(i)}(\eta) = \sum_{l} C^{(l)}_{m,n} \frac{(n-m)!}{(n+m)!} \cos(m\varphi_{i}) P_{n}^{(m)}(\cos \theta_{i}) \left( \eta_{0i}^{(m)} \right)^{n} \frac{(n+1)-\alpha_{0i}}{n+\alpha_{0i}} \]

Here the coefficient of the series is

\[ C^{(i)}_{m,n} = \sum_{l} C^{(l)}_{m,n} \frac{(n-m)!}{(n+m)!} \cos(m\varphi_{i}) P_{n}^{(m)}(\cos \theta_{i}) \left( \eta_{0i}^{(m)} \right)^{n} \frac{(n+1)-\alpha_{0i}}{n+\alpha_{0i}} \]

In the particular case of active centers located on the same diameter, the axis \( z \) is directed along this diameter (see figure 2).

Figure 2. Coordinate system with active centers along the diameter.

In this case, in the formula (18) \( m = 0 \), associated Legendre polynomials are converted to ordinary Legendre polynomials \( P_{n}(x) \), and the temperature distribution inside the pellet is described by formula

\[ \Theta(\eta) = \sum_{l} \eta_{0i}^{(m)} \frac{1}{\sqrt{\eta_{0i}^{(m)}} \cos \theta_{i} + \left( \eta_{0i}^{(m)} \right)_{n}} + \sum_{n=0}^{\infty} C^{(i)}_{n} \eta_{0i}^{(m)} P_{n}(\cos \theta_{i}) \]

\[ C^{(i)}_{n} = \left( \eta_{0i}^{(m)} \right)^{n} \frac{(n+1)-\alpha_{0i}}{n+\alpha_{0i}} \]

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Here $\theta$ is the polar angle of the deviation of the observation point radius vector $\eta$ from the axis $z$ passing through the active centers.

5. Self-consistent field method

To calculate the temperature of the active center $\Theta_0^{(i)}$, we apply the idea of the self-consistent field method. The total temperature distribution in the volume of the granule is represented by the sums (14) and (18). We average the temperature distribution over the volume of a single active reaction center, whose diameter is much smaller than the diameter of the granule $d_{gr} \ll d_{co}$ and distance between centers. As a result of averaging, taking into account the smallness of the volume of the active center, we obtain the average temperature of the active center.

We rewrite formula (19) for the temperature distribution inside the granule in the form

$$\Theta(\eta) = \sum_{i=1}^{N_S} \Xi^{(i)}_{0} \left\{ \frac{1}{|\eta - \eta^{(i)}_{0}|} + \sum_{j=0}^{n} \sum_{m,n} C^{(j)}_{m,n} \cos \left[ m (\varphi - \varphi^{(j)}_{0}) \right] P^m_n (\cos \theta) \eta^{(i)}_{m,n} \right\}$$

\hspace{1cm} (20)

![Diagram](image)

**Figure 3.** The scheme of averaging over the volume of the active reaction centre $\eta_{0}^{(i)}$.

We find the temperature averaged over the volume of the active center with the coordinate $\eta_{0}^{(i)}$

$$\Theta_0^{(i)} = \frac{1}{V_0 V_{0'}} \int \Theta(\eta_0^{(i)} + \eta') d\eta'$$

Here $V_0$ is the volume of the active center, $d\eta'$ denotes differential of the active center volume.

We calculate the integral over the volume of the active center with the radius-vector $\eta_{0}^{(i)}$. Rewriting the temperature distribution in the volume of the active center

$$\Theta(\eta_0^{(i)} + \eta') = \sum_{i=1}^{N_S} \Xi^{(i)}_{0} \left\{ \frac{1}{|\eta_0^{(i)} - \eta_{0}^{(i)} + \eta'|} \right\}$$
\[ + \sum_{n=0}^{N} \sum_{m=0}^{M} C_{m,n}^{(i)} \cos \left( m \left( \varphi_{0}^{(i)} - \varphi_{0}^{(i)} + \varphi' \right) \right) p_{n}^{m} \left( \cos \left( \theta_{0}^{(i)} + \theta' \right) \right) \left( \eta_{0}^{(i)} + \eta' \right)^{n} \] 

(21)

In the second term of the formula (21) for the distribution of temperature near the center \( \eta_{0}^{(i)} \) can be put \( \eta = \eta_{0}^{(i)} + \eta' \approx \eta_{0}^{(i)} \). In this case, averaging over the volume of the granule of the second term in formula (21) is equal to

\[ \sum_{n=0}^{N} \sum_{m=0}^{M} C_{m,n}^{(i)} \frac{1}{V_{0}V_{0}'} \int \cos \left( m \left( \varphi_{0}^{(i)} - \varphi_{0}^{(i)} + \varphi' \right) \right) p_{n}^{m} \left( \cos \left( \theta_{0}^{(i)} + \theta' \right) \right) \left( \eta_{0}^{(i)} + \eta' \right)^{n} \, d\eta' \]

\[ \approx \sum_{n=0}^{N} \sum_{m=0}^{M} C_{m,n}^{(i)} \cos \left( m \left( \varphi_{0}^{(i)} - \varphi_{0}^{(i)} \right) \right) p_{n}^{m} \left( \cos \left( \theta_{0}^{(i)} \right) \right) \left( \eta_{0}^{(i)} \right)^{n} \]

Calculate the integral over the volume of the spherical center from the first term on the right-hand side of the formula (21)

\[ \frac{1}{V_{0}V_{0}'} \int \frac{d\eta'}{\left| \eta_{0}^{(i)} - \eta_{0}^{(i)} + \eta' \right|} \]

In the last formula we distinguish two different expressions. The first expression describes the contribution to the temperature of the active center when the coordinates coincide \( \eta_{0}^{(i)} = \eta_{0}^{(i)} \). This corresponds to a single active center in the granule (see figure 3 (a)). For a single active center, we calculate the integral as follows

\[ \frac{1}{V_{0}V_{0}'} \int \frac{d\eta'}{\left| \eta_{0}^{(i)} - \eta_{0}^{(i)} + \eta' \right|} = \frac{3}{4\pi(\delta_{0}/2)^{3}} \int_{0}^{\delta_{0}^{2}/2} \eta_{0}'^{2} d\eta' = \frac{3}{\delta_{0}} \]

Here \( \delta_{0} = d_{0}/d_{g} \ll 1 \) is the relative diameter of the active center.

For distinct coordinates of the centers \( \eta_{0}^{(i)} \neq \eta_{0}^{(i)} \) (see figure 3 (b)), we write down the relation between the vectors \( \eta - \eta_{0}^{(i)} = \eta_{0}^{(i)} - \eta_{0}^{(i)} + \eta' \). Averaging over the volume of the center in formula (21) is carried out under the condition that \( \eta_{0}^{(i)} - \eta_{0}^{(i)} + \eta' \approx \eta_{0}^{(i)} - \eta_{0}^{(i)} \)

\[ \frac{1}{V_{0}V_{0}'} \int \frac{d\eta'}{\left| \eta_{0}^{(i)} - \eta_{0}^{(i)} + \eta' \right|} \approx \frac{1}{V_{0}V_{0}'} \int \frac{d\eta'}{\left| \eta_{0}^{(i)} - \eta_{0}^{(i)} \right|} = \frac{1}{\left| \eta_{0}^{(i)} - \eta_{0}^{(i)} \right|} \]

Collecting the obtained results, we find the temperature of the active center, expressed through the overall temperature distribution inside the granule

\[ \Theta_{0}^{(i)} = \sum_{i=1}^{N} \frac{\Xi_{a}^{(i)}}{\left| \eta_{0}^{(i)} - \eta_{0}^{(i)} \right|} + \sum_{i=1}^{N} \frac{\Xi_{a}^{(i)}}{\delta_{0}} + \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} C_{m,n}^{(i)} \cos \left( m \left( \varphi_{0}^{(i)} - \varphi_{0}^{(i)} \right) \right) p_{n}^{m} \left( \cos \left( \theta_{0}^{(i)} \right) \right) \left( \eta_{0}^{(i)} \right)^{n} \] 

(22)

We calculate the power of heat generation in the active center by the formula (9). Thus, we obtain a system of transcendental algebraic equations (22) for calculating the temperature of active centers.
6. Equations for the concentration of synthesis gas at active reaction centres

Similarly to temperature, we obtain a system of equations for the concentration of carbon monoxide and hydrogen on active sites.

The system of equations for the concentration of CO on active reaction centers has the form

$$
\Psi_{CO}^{(j)} = \sum_{i=1}^{N_i} \left[ \frac{\Xi_{CO}^{(j)}}{\eta_{0}^{(j)} - \eta_{i}^{(j)}} \right] + 3 \frac{\Xi_{CO}^{(j)}}{\delta_0} + \sum_{i=1}^{N_i} \sum_{m=0}^{\infty} F_{m,n_{CO}}^{(j)} \cos \left( m \left( \varphi_0^{(j)} - \varphi_i^{(j)} \right) \right) P_n^m \left( \cos \left( \Theta_0^{(j)} \right) \right) \left( \eta_0^{(j)} \right)^n \right] 
$$

(23)

Here the coefficients of the series are equal to

$$
F_{m,n_{CO}}^{(j)} = \varepsilon_{m} \left( n - m \right)! \frac{P_n^m \left( \cos \left( \Theta_0^{(j)} \right) \right) \left( \eta_0^{(j)} \right)^n \left( n + 1 \right) - \beta_{CO}^n}{n + \beta_{CO}^n}
$$

The rate of consumption of carbon monoxide is calculated by the formula (11).

The equation system for calculating H$_2$ concentration has the form

$$
\Psi_{H_2}^{(j)} = \sum_{i=1}^{N_i} \left[ \frac{\Xi_{H_2}^{(j)}}{\eta_{0}^{(j)} - \eta_{i}^{(j)}} \right] + 3 \frac{\Xi_{H_2}^{(j)}}{\delta_0} + \sum_{i=1}^{N_i} \sum_{m=0}^{\infty} G_{m,n_{H_2}}^{(j)} \cos \left( m \left( \varphi_0^{(j)} - \varphi_i^{(j)} \right) \right) P_n^m \left( \cos \left( \Theta_0^{(j)} \right) \right) \left( \eta_0^{(j)} \right)^n \right] 
$$

(24)

Here coefficients of the series are equal to

$$
G_{m,n_{H_2}}^{(j)} = \varepsilon_{m} \left( n - m \right)! \frac{P_n^m \left( \cos \left( \Theta_0^{(j)} \right) \right) \left( \eta_0^{(j)} \right)^n \left( n + 1 \right) - \beta_{H_2}^n}{n + \beta_{H_2}^n}
$$

The rate of consumption of hydrogen is represented by the formula (12).

7. The solution of nonlinear equations by the method of establishing

The system of transcendental algebraic equations (22)–(24) is solved by the method of establishment by reduction to the system of ordinary differential equations (ODE) of relaxation type.

ODE for temperature at the active center has the form

$$
\tau_0 \frac{d\Theta_0^{(j)}}{dr} = \sum_{i=1}^{N_i} \left[ \frac{\Xi_{\Theta_0}^{(j)}}{\eta_{0}^{(j)} - \eta_{i}^{(j)}} \right] + 3 \frac{\Xi_{\Theta_0}^{(j)}}{\delta_0} + \sum_{i=1}^{N_i} \sum_{m=0}^{\infty} \Xi_{m,n_{\Theta_0}}^{(j)} \cos \left( m \left( \varphi_0^{(j)} - \varphi_i^{(j)} \right) \right) P_n^m \left( \cos \left( \Theta_0^{(j)} \right) \right) \left( \eta_0^{(j)} \right)^n \right] - \Theta_0^{(j)}
$$

ODE for CO concentration at the active center is

$$
\tau_0 \frac{d\Psi_{CO}^{(j)}}{dr} = \sum_{i=1}^{N_i} \left[ \frac{\Xi_{\Psi_{CO}^{(j)}}^{(j)}}{\eta_{0}^{(j)} - \eta_{i}^{(j)}} \right] + 3 \frac{\Xi_{\Psi_{CO}^{(j)}}^{(j)}}{\delta_0}
$$
\[ + \sum_{i=1}^{N} \Xi_{i}^{(i)} \left( \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} R_{m,n}^{(i)} \cos \left( m \left( \phi_{i}^{(i)} - \phi_{0}^{(i)} \right) \right) b_{m}^{(i)} \left( \cos \left( \theta_{i}^{(i)} \right) \right) \left( \eta_{0}^{(i)} \right)^{n} \right) - \Psi_{CO}^{(i)} \]

ODE for \( H_{2} \) concentration at the active center

\[
\tau_{0} \frac{d\Psi_{H_{2}}^{(i)}}{dt} = \sum_{i \neq j}^{N} \Xi_{H_{2}}^{(i,j)} \left( \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} R_{m,n}^{(i,j)} \cos \left( m \left( \phi_{0}^{(i)} - \phi_{0}^{(j)} \right) \right) b_{m}^{(i,j)} \left( \cos \left( \theta_{0}^{(i)} \right) \right) \left( \eta_{0}^{(j)} \right)^{n} \right) + 3 \frac{\Xi_{H_{2}}^{(i)}}{\delta_{0}}
\]

\[
+ \sum_{i=1}^{N} \Xi_{H_{2}}^{(i)} \left( \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} R_{m,n}^{(i)} \cos \left( m \left( \phi_{0}^{(i)} - \phi_{0}^{(i)} \right) \right) b_{m}^{(i)} \left( \cos \left( \theta_{0}^{(i)} \right) \right) \left( \eta_{0}^{(i)} \right)^{n} \right) - \Psi_{H_{2}}^{(i)}
\]

Here \( \tau_{0} \) is the relaxation parameter chosen from the stability condition of the algorithm for solving the ODE.

We also give formulas for calculating the distribution of temperature and concentration of synthesis gas in the case of active centers located along the diameter of the granule. Equations for temperature of the active centers have the form

\[
\tau_{0} \frac{d\Theta_{CO}^{(i)}}{d\xi} = \sum_{i \neq j}^{N} \Xi_{CO}^{(i,j)} \left( \sum_{n=0}^{\infty} \left( n+1 \right) - \frac{\alpha_{CO}^{*}}{n+\alpha_{0}} \left( \eta_{0}^{(i,j)} \right)^{n} \right) \left( \eta_{0}^{(i,j)} \right)^{n}
\]

\[
+ \Xi_{CO}^{(i,j)} \left( 3 \frac{\eta_{CO}^{(i,j)}}{\delta_{0}} + \frac{\eta_{CO}^{(i,j)}}{n+\alpha_{CO}^{*}} \left( \eta_{0}^{(i,j)} \right)^{n} \right) - \Theta_{CO}^{(i,j)}
\]

Equations for concentrations of CO at the active centers we write as

\[
\tau_{0} \frac{d\Psi_{CO}^{(i)}}{d\xi} = \sum_{i \neq j}^{N} \Xi_{CO}^{(i,j)} \left( \sum_{n=0}^{\infty} \left( n+1 \right) - \frac{\beta_{CO}^{*}}{n+\beta_{CO}^{*}} \left( \eta_{0}^{(i,j)} \right)^{n} \right) \left( \eta_{0}^{(i,j)} \right)^{n}
\]

\[
+ \Xi_{CO}^{(i,j)} \left( 3 \frac{\eta_{CO}^{(i,j)}}{\delta_{0}} + \frac{\eta_{CO}^{(i,j)}}{n+\beta_{CO}^{*}} \left( \eta_{0}^{(i,j)} \right)^{n} \right) - \Psi_{CO}^{(i,j)}
\]

Equations for \( H_{2} \) concentration looks like that

\[
\tau_{0} \frac{d\Psi_{H_{2}}^{(i)}}{d\xi} = \sum_{i \neq j}^{N} \Xi_{H_{2}}^{(i,j)} \left( \sum_{n=0}^{\infty} \left( n+1 \right) - \frac{\beta_{H_{2}}^{*}}{n+\beta_{H_{2}}^{*}} \left( \eta_{0}^{(i,j)} \right)^{n} \right) \left( \eta_{0}^{(i,j)} \right)^{n}
\]

\[
+ \Xi_{H_{2}}^{(i,j)} \left( 3 \frac{\eta_{H_{2}}^{(i,j)}}{\delta_{0}} + \frac{\eta_{H_{2}}^{(i,j)}}{n+\beta_{H_{2}}^{*}} \left( \eta_{0}^{(i,j)} \right)^{n} \right) - \Psi_{H_{2}}^{(i,j)}
\]

The method of solving a system of transcendental algebraic equations by reducing to the system of ODE is an effective technique that allows one to obtain the roots which are stable to small perturbations.
8. Homogeneous model of the catalyst pellet

In order to illustrate the qualitative features of the model of local active centres, we also present the results of calculations for a homogeneous model of a catalyst granule. In a homogeneous model, chemical reactions take place at each point in the volume of the pellet. In a homogeneous model, equations for the temperature and the concentration of the components of the synthesis gas inside the granule have the form

\[ \rho_{gr} c_{gr} \frac{\partial T_{gr}}{\partial t} = \lambda_{gr} \Delta T_{gr} + Q_{FT} \frac{m_{CO}}{V_{gr}} \Phi_{CO} (T_{gr}, P_{CO}, P_{H_2}) \]

\[ \frac{\partial C_{CO}}{\partial t} = D_{CO} \Delta C_{CO} - \frac{m_{CO}}{V_{gr}} \Phi_{CO} (T_{gr}, P_{CO}, P_{H_2}) \]

\[ \frac{\partial C_{H_2}}{\partial t} = D_{H_2} \Delta C_{H_2} - \zeta_{n_{H_2}/CO} \frac{m_{CO}}{V_{gr}} \Phi_{CO} (T_{gr}, P_{CO}, P_{H_2}) \]

Here \( V_{gr} = \pi d_{gr}^3 / 6 \) is volume of the granule.

On the granule surface the boundary conditions for balance equations coincide with formulas (3)–(7). For a spherically symmetric granule, we also set the symmetry conditions in the center of the granule

\[ \left. \frac{\partial T_{gr}}{\partial r} \right|_{r=0} = 0 , \quad \left. \frac{\partial C_{CO}}{\partial r} \right|_{r=0} = 0 , \quad \left. \frac{\partial C_{H_2}}{\partial r} \right|_{r=0} = 0 \]

The steady-state temperature and gaseous concentration distributions were found by integrating the implicit method above system of equation with account boundary conditions.

9. Calculation results

Due to the peculiarities of manufacturing technology of millimetre porous catalyst pellets with embedded dispersed metallic cobalt, it is impossible to arrange micro-particles in strictly defined points of the granule. Coordinates microparticles we define as follows. Along the polar \( \theta \) and azimuth angles \( \phi \) the particles are randomly distributed according to a uniform law. The coordinates of the particles along the radius of the granule are calculated by the formula

\[ \eta_{i}^{(j)} = (1 - \delta_{o}) \left( \frac{i-1}{N_{o} - 1} \right)^{k} \]  \hspace{1cm} (25) \]

The value of the degree \( k \) can controlled the density of distribution of cobalt microparticles in the volume of the granule.

Figure 4 shows the actual arrangement of the microparticles for the two values of the exponent \( k \) in the formula (25). It is seen that, depending on the magnitude of the exponent, the concentration of microparticles in the volume varies significantly.

In the calculations we used the values of chemical synthesis kinetics constants borrowed from [32]. The calculation is carried out without taking into account liquid products: this is the so-called "dry catalyst" approximation. The rate of synthesis of gas is 3000 h\(^{-1}\). The heat transfer coefficient is estimated from the cross section of the catalyst bed with a porosity of 0.6.
Figure 4. An example of the actual location of active reaction centers in the catalyst pellet for two values of the exponent: $k = 1$ (a); $k = 9$ (b).

The real catalyst particles are cylinders with a diameter of 3 mm and a height of 2 mm. The radius of the effective sphere is calculated by the volume of the granule. The thermophysical properties of CO and H$_2$ and the diffusion coefficients are determined in accordance with the recommendations of [33]. The mass fraction of cobalt in the granule varies in the range 10-18%. The thermal conductivity coefficient of the catalyst pellet is 4 W/(m K).

Figure 5. Temperature distribution in the cross section of the granule with single active centre: distribution of dimensionless temperature in the cross section passing through the diameter with the active centre (a); temperature distribution along the diameter passes through the active centre; dashed lines denote diameter of cobalt microparticle (b).

For synthesis reactions with exothermic chemical reactions, there is a critical temperature, exceeding which leads to a loss of thermal stability – heat explosion. As a result, there is a significant overheating of the active centers of the granule in comparison with the temperature of the surrounding medium. Below the critical temperature in the reactor tube, active reaction centers are superheated compared to the temperature in the reactor tube slightly, only a few degrees. Exceeding the critical
value of temperature of synthesis gas in the reactor tube leads to a sharp increase in the temperature of the active centers. This situation is dangerous and can lead to a thermal explosion of the reactor.

**Figure 6.** Distribution of temperature in the granule: temperature of the active centers (a); 1 - temperature along the diameter with centers, 2 - temperature on a diameter perpendicular (b).

**Figure 7.** Dimensionless temperature in the cross section with active centers.

We present the results of calculations for two model cases and results of simulation the real catalyst granules. One of model case is single active center, and second model case is the system of active centers located on the same diameter of the granule. In the second model case we consider a relatively small number (of the order of a dozen) of active centers along the diameter of the granule. Therefore, the total heat capacity of the pellet, we redistribute in a limited number of centers. With the selected parameters of catalytic reactor, the thermal explosion begins at a temperature about 250°C.

Figure 5 shows the temperature distribution in the cross section granules with a single active center. It is seen that the surface temperature of the granules slightly overheated; however, temperature of the active center achieves a substantial amount. Note that at the thermal explosion the limiting role belongs to the carbon monoxide. The concentration of carbon monoxide on the active centers is close to zero.
Figure 8. Influence of the inhomogeneity location of the active centers. Lines represent the temperature distribution along the various diameters of granules.

Figure 6 (a) presents the temperature of the active centers located on the same diameter. Figure 6 (b) illustrates the temperature distribution of the granule along the diameter with active centers and along the perpendicular diameter. From the figure 6 it also follows that the reaction centers have a substantially higher temperature than the bulk of the granules.

Understanding of the distribution of the dimensionless temperature inside the granule gives the figure 7. It is also possible to conclude that the surface temperature of the pellets did not give complete information about the actual temperature of the active centers.

In the case of three-dimensional arrangement of active centers, the pattern of temperature distribution inside the granule becomes more complex. Grouping cobalt microparticles in the center of the granules leads to significant overheating (see figure 8 (a)).

Figure 9. Illustration of the inhomogeneity of the temperature distribution in a granule with point reaction centres: the sphere in the space with active centres (a); temperature distribution on the surface of the sphere (b).
It can be seen from figure 8 (a) that the central region of the granule is superheated much higher than the peripheral part of the granule close to the boundary. Increasing the concentration of cobalt in the central part of microparticles granules is achieved at degree value in the formula (25) $k$.

Uniform distribution of cobalt microparticles in the granule volume, or increase their concentration near the boundary is reached at a value of exponent in the formula (25) $k \gg 1$. In this case, the local regions of overheating are almost uniformly distributed over the volume of the granule (see figure 8 (b)).

From figure 8 we can generally conclude that at thermal explosion the active centres of reaction overheated considerably higher than the surface of the granule.

Qualitative representation of the substantial heterogeneity in the temperature distribution in the volume of granule gives the figure 9.

Figure 8 (a) represents a sphere immersed in a system of point heat-generating centres. At a radius of the sphere at the each point of the sphere surface is deposited local temperature. From figure 9 (b), it is possible to see local superheated regions within the catalyst granule.

![Figure 10](attachment:temperature_distribution.png)

**Figure 10.** Distribution of temperature in the granule in the frame of homogeneous model.

A fundamentally different picture is obtained within a homogeneous model. For homogeneous model thermal explosion, which is a sharp increase in the temperature of the granule, occurs at a more higher temperature, about 270°C instead of 250°C in the case of model of local centres. In a homogeneous model between the surface temperature and the temperature in the volume of the granule, there is a unique relationship (see Figure 10).

Unlike traditional homogeneous model for catalyst granules with point reaction centres requires a fundamentally new way of describing the processes of heat and mass transfer.

10. **Conclusions**

A self-consistent model for the calculation of stationary temperature distributions and CO and H$_2$ concentrations inside a porous granule with discrete located active cobalt-based synthesis centres is presented.

The actual chemical reaction kinetics Fischer-Tropsch synthesis, determined experimentally on the fine-grained cobalt was taken into account. The value of the critical temperature above which a thermal explosion occurs is established.
It is shown that when the critical temperature of the reactor tube is reached, a significant overheating of active synthesis centres occurs as a jump wise. In this case the catalyst pellet surface is overheated considerably less.

On the basis of calculations a fundamental difference in the distribution of temperature and concentration in the homogeneous model and in the model of active centres is established.

The calculation procedure can be used to create a new generation of catalysts, customizable for specific product composition.

Note that the results presented here were obtained for the first time.

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12. Appendices
Here we present the evaluation of the relative distance between the active centres of the catalyst pellet.

The mass of the granule together with cobalt is

$$m_{gr} = m_{Co} + m_{cer}$$

Here $m_{gr}$, $m_{Co}$, $m_{cer}$ are mass of granule, cobalt and chemically passive ceramic base.

Given by the mass fraction of cobalt $\gamma_{Co} = m_{Co}/m_{gr}$, we find the expression of the cobalt mass through the mass of the ceramic base of the granule

$$m_{Co} = \frac{\gamma_{Co}}{1 - \gamma_{Co}} m_{cer}$$

Mass of cobalt and ceramic base are $m_{cer} = \rho_{cer} V_{cer}$, $m_{Co} = \rho_{Co} V_{Co}$ ($\rho_{cer}$, $\rho_{Co}$ are densities of ceramics and cobalt; $V_{cer}$, $V_{Co}$ are volumes of ceramic and cobalt). The volume of the granule is $V_{gr} = V_{Co} + V_{cer}$. Volumes of cobalt and ceramic base through the volume of the granule are

$$V_{Co} = \frac{\gamma_{Co} \rho_{cer}}{\rho_{Co} (1 - \gamma_{Co}) + \gamma_{Co} \rho_{cer}} V_{gr}, \quad V_{cer} = \frac{\rho_{Co} (1 - \gamma_{Co})}{\rho_{Co} (1 - \gamma_{Co}) + \gamma_{Co} \rho_{cer}} V_{gr}$$

The number of microparticles of cobalt in the granule is $N_{Co} = V_{Co}/V_{Co}$ ($V_{Co} = \pi d_{Co}^3/6$ is volume of one cobalt microparticle). To estimate the characteristic distance between the cobalt microparticles, we use the effective cell model. Ceramic base volume per one particle of cobalt is equal $v_{cer} = V_{cer}/N_{Co} = \pi (d_{cer}^3 - d_{Co}^3)/6$ (see figure 11).

The effective distance between microparticles is estimated as

$$\Delta_{cer} = d_{cer} - d_{Co}, \quad \Delta_{cer} = \left[d_{cer}^3 + \frac{6 V_{cer}}{\pi N_{Co}}\right]^{1/3} - d_{Co}$$

Using the expressions obtained earlier, we write down a formula for estimating the distance between cobalt microparticles
$$\Delta_{\text{cer}} = d_{\text{Co}} \left\{ \frac{1 + \frac{\rho_{\text{Co}}}{\rho_{\text{cer}}} \left( \frac{\gamma_{\text{Co}}}{\gamma_{\text{cer}}} \right)^{1/3}}{1 - \frac{\rho_{\text{Co}}}{\rho_{\text{cer}}} \left( \frac{\gamma_{\text{Co}}}{\gamma_{\text{cer}}} \right)^{1/3}} - 1 \right\}$$

Figure 11. Model of effective cells for estimating the distance between active microparticles.

Let us give an example. Let the granule diameter be $d_{\text{gr}} = 2$ mm, the diameter of the cobalt microparticles is $d_{\text{Co}} = 35 \mu$m, the density of the ceramic is $\rho_{\text{cer}} = 800$ kg/m$^3$ and the mass fraction of cobalt is $\gamma_{\text{Co}} = 10\%$. In this case, number of cobalt microparticles $N_{\text{Co}} \approx 1800$ and the distance between the microparticles $\Delta_{\text{cer}}/d_{\text{Co}} \approx 4$.

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