

MODELING POLYACRYLONITRILE PYROLYSIS.

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Abstract.

The formulation of the polyacrylonitrile pyrolysis problem, the designing of its process and the problem solution are discussed. The pyrolysis is considered as a double step process when the formation of a liquid phase is excluded, that is the initial substance and the coke obtained are powders. Three main reactions are considered: a) with the evolution of ammonia; b) with the evolution of hydrogen cyanide; c) with the evolution of hydrogen. The latter two reactions are sequential, and the reactions a) and b) are parallel. The problem is formulated as one-dimensional. The equations of energy, masses or concentrations, porosity and thermal conductivity are proposed. The mathematical model of the carbonization process is designed using the above reactions (a, b and c). The equations received are calculated by the Runge - Cutta method. The results of calculations were confirmed by the tendency of experimental data changes.

Nomenclature :

χ_{ins} - the volume fraction of
intermediate substances;

χ_{exc} - the volume fraction of
the changing coke during the pyrolysis;

χ_{ps} - the volume fraction of
initial passive substances;

ρ - the density;

P - the pressure;

c_p, c_v - the isobaric and isochoric
heat capacities;

α - the mass concentration;

ψ - the porosity;

ν - the rate;

E - the activation energy;

H - the enthalpy;

R - the gaseous constant;

λ - the thermal conductivity
coefficient;

T - the temperature;

m - the mass;

W - the volume;

y - the space coordinate;

a - the heat transfer coefficient;

t - the time.

Introduction.

The polyacrylonitrile (PAN) is one of the main types of substances used for obtaining carbon fibers. According to the structure of the polymer and its intermediates the carbon fiber can be obtained by the pyrolysis. The pyrolysis is considered as a double step process when the formation of a liquid phase is excluded. In other words the initial substance (PAN) is destructed with the formation of a solid residue (coke), gaseous substances and intermediate solid substances. The PAN pyrolysis process proceeds at 673-1073 K. At these temperatures the main reactions of a polymer thermodestruction take place, and besides intermediate solid substances are formed. The latter participate in the formation of a fiber carbon structure.

The pattern of physico-chemical processes in a warmed up layer of the material condensed phase.

Physico-chemical processes which proceed in a warmed up surface layer of the material condensed phase are considered (Fig.1).

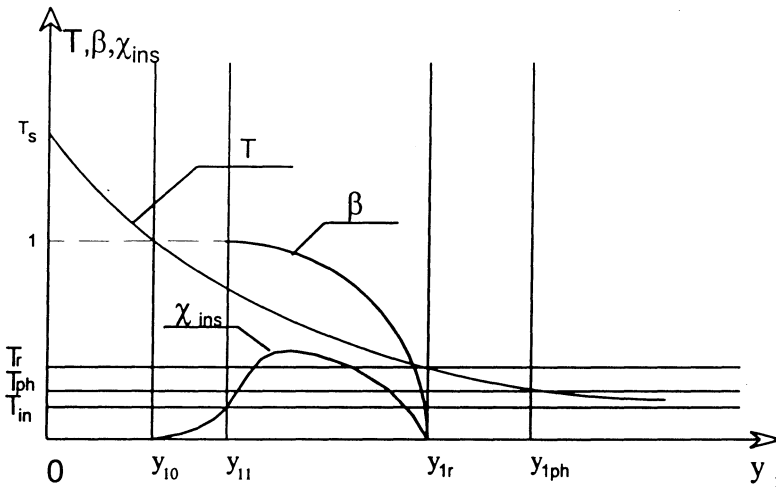


Fig.1 Scheme of process parameter changes (parameters: the temperature, the fraction of a destructed active component β and the fraction of intermediate substances χ_{ins}) in relation of coordinate y_1 in the warmed up layer of the material.

In this case the heat comes in the material surface layer from outside surroundings. The temperature profile which depends on the coordinate

y_1 directed into the material is shown in fig.1. However such character of the process and the temperature changes can be regarded as a particular case.

The warmed up layer adjoining the surface of the material is a volume with a markedly changing temperature compared to the layer inside the material whose temperature equals the initial value $\dot{O}=\dot{O}_{in}=293\text{ K}$.

Polymorphic transformations inside the material are taken into account when $\dot{o}_1=\dot{o}_{1tr}$ and $\dot{O}=\dot{O}_{tr}$ and at $\dot{o}_1=\dot{o}_{1tr}$ the pyrolysis starts.

Let us suppose that the initial material contains an active component participating in the reaction and undergoing transformations, but the passive component is not changed during the pyrolysis.

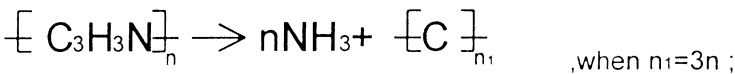
It's known [1] that the polyacrylonitrile powder heated to $\dot{O}=\dot{O}_{tr}=523\text{ K}$ is transformed in the cyclic polymer. In other words at this temperature the cyclization process takes place with the participation of polyacrylonitrile. As a result the material becomes more compact than the initial polymer. The cyclization process is accompanied by emitting the heat, increasing the thermal conductivity and by changing other material properties. Thermophysical parameters before and after the polymorphic transformation are given in the Table.

Table. Thermophysical characteristics of polyacrylonitrile before and after the polymorphic transformation.

Characteristics	Density $\frac{\text{kg}}{\text{m}^3}$	Conductivity $\frac{\text{kW}}{\text{m K}}$	Heat capacity $\frac{\text{kJ}}{\text{kg K}}$	Enthalpy $\frac{\text{kJ}}{\text{mol}}$
Before the polymorphic transformation	1150	0.09	1.2	—
After the polymorphic transformation	1500	0.11	2.2	180

The temperature of the beginning of a chemical destruction equals $\dot{O}=\dot{O}_d=673\text{ K}$. At this the combination of sequential-parallel chemical reactions starts. At first two parallel reactions proceed:

1) the destruction with the isolation of ammonia

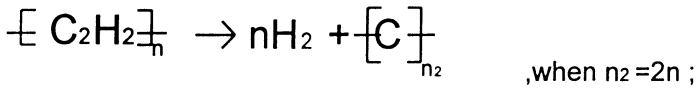


2) the destruction with the isolation of hydrogen cyanide



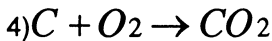
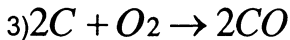
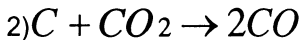
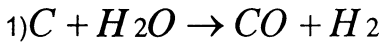
The temperature of the beginning of the first reaction is 673 K. This reaction proceeds with the destruction of the initial substance and is accompanied by the grafitization. At the same time the second reaction begins at 723 K with the

formation of an intermediate substance $\left[\text{CH}=\text{CH} \right]_n$, which is active in the cyclization reaction, (the third reaction) that starts at 873 K.



Thus three different gases (NH_3 , HCN , H_2) are evolved from the material. These gases are formed in the material volume, then they are filtered through the pores formed to the material surface and enter the environment.

Simultaneously oxidizers are diffused from the surroundings to the material surface. The oxidizers interact with the carbon net formed during the polyacrylonitrile pyrolysis. The following heterogeneous chemical reactions proceed in parallel in the material surface:



The rate of these reactions promotes the carbon layer decrease between the material surface and the coordinate δ_1 equaled to δ_{10} . This decrease is small. Therefore let us assume that the thickness of the carbon layer formed is constant so that the thickness of another layer in the material volume at stationary conditions.

Furthermore it is supposed that the polyacrylonitrile - based material contains passive substances whose volume fraction is known and does not change at the heating.

The designing of the mathematical model.

The mathematical model of the polyacrylonitrile pyrolysis under the above assumptions is designed using the data of physico-chemical processes.

The material ablation rate is determined according to the following equation

$$u\rho_{chc} = \sum_{i=1}^4 m_{is} \left(1 + \frac{b_i \mu_{B_i}}{a_i \mu_A}\right)^{-1} \quad (1);$$

where m_{is} - the mass rate of the carbon heterogeneous interactions with i -oxidizer reactants ($i=1,2,3,4$), \bar{n} - corresponding to the material surface unit .

u - the material ablation rate ,

ρ_{chc} - the density of the changing coke ,

b_i, a_i - stoichiometric coefficients ,

μ_A - the carbon molecular mass ,

μ_{B_i} - molecular masses of water vapours , oxygen and carbon oxide.

Stationary equations for the parameters of gaseous substances (formed inside the material in the process of its destruction) are represented in coordinates connected with the changing material surface. They are received on the basis of conservation laws :

The continuity equation

$$\frac{d}{dy_1} (v_g - u) \psi \rho_g = \sum_{i=1}^3 m_{ig} \quad (2)$$

The concentration equation

$$\frac{d}{dy_1} (u - v_g) \alpha_i \psi \rho_g = -m_{ig} \quad i=1:3 \quad (3)$$

The equation obtained on the basis of the law of pulse conservation

$$\frac{d}{dy_1} [(v_g - u) v_g \psi \rho_g + \psi P] = -\tau + P \frac{d\psi}{dy_1} \quad (4)$$

The equation obtained on the basis of energy equation .

$$\begin{aligned} & \frac{d}{dy_1} \lambda_m \frac{dT}{dy_1} - \frac{d}{dy_1} \psi \rho_g v_g H + u \frac{d}{dy_1} [\psi \rho_g E + (1 - \psi)(c\rho)_m T] = \\ & = - \sum_{i=1}^3 m_i Q_i \end{aligned} \quad (5)$$

where m_i - the specific influx of gaseous substances corresponding to the volume unit as a result of the i -reaction proceeding

$$\begin{aligned} m_1 &= (1 - \beta)^{m_1} K_1 e^{\left(-\frac{E_1}{RT}\right)} \left(1 - \psi - \chi_{chc} - \chi_{ins} - \alpha_{ps} \frac{\rho_o}{\rho_{ps}}\right) dW \\ m_2 &= (1 - \beta)^{m_2} K_2 e^{\left(-\frac{E_2}{RT}\right)} \left(1 - \psi - \chi_{chc} - \chi_{ins} - \alpha_{ps} \frac{\rho_o}{\rho_{ps}}\right) dW \\ m_3 &= \chi_{ins}^{m_3+1} + K_3 e^{\left(-\frac{E_3}{RT}\right)} \end{aligned}$$

$$\beta = 1 - \frac{\rho_m - \psi \rho_g - \chi_{chc} \rho_{chc} - \chi_{ins} \rho_{ins} - \alpha_{ps} \rho_o}{\rho_o - \psi \rho_{gin} - \alpha_{ps} \rho_o}$$

τ - tangential stresses of the resistance force are determined using the Cozenn - Carman formula :

$$\tau = A \frac{\psi^2}{(1 - \psi)^2}$$

The resistance to the gaseous substance moving along pores is considered as proportional to the cross - section area of an elemental volume , and the tangential stress is related to the length unit and the cross -section area unit :

$$E = \frac{v_g^2}{2} + c_v T$$

$$H = E + \frac{P}{\rho_g} = \frac{v_g^2}{2} + c_p T$$

$$c_p - c_v = R$$

The following equation is proposed for the calculation of porosity ψ taking into account pyrolysis reactions the mentioned above .

$$\begin{aligned}
 -u \frac{d\psi}{dy_1} = & \left[\left(\frac{1}{\rho_a} - \frac{1}{\rho_{chc}} - \frac{1}{1 + \frac{b_1 \mu_{B_1}}{c_1 \mu_{C_1}}} \right) (1 - \beta)^{m_1} K_1(T) + \right. \\
 & \left. + \left(\frac{1}{\rho_a} - \frac{1}{\rho_{ins}} - \frac{1}{1 + \frac{b_2 \mu_{B_2}}{c_2 \mu_{C_2}}} \right) (1 - \beta)^{m_2} K_2(T) \right] \times \\
 & \times \left(1 - \psi - \chi_{chc} - \chi_{ins} - \alpha_{ps} \frac{\rho_0}{\rho_{ps}} \right) + \\
 & + \left(\frac{1}{\rho_{ins}} - \frac{1}{\rho_{chc}} - \frac{1}{1 + \frac{b_3 \mu_{B_3}}{c_3 \mu_{C_1}}} \right) \chi^{m_3+1}_{ins} K_3(T) \quad (6)
 \end{aligned}$$

For the volume fraction calculation of the changing coke and intermediate substances upon which the porosity depends the following equations are received :

The equation for the volume fraction of the changing coke;

$$\begin{aligned}
 -u \frac{d\chi_{chc}}{dy_1} &= \frac{(1-\beta)^{m_1} K_1(T)}{1 + \frac{b_1\mu_{B_1}}{c_1\mu_{C_1}}} \left(1 - \psi - \chi_{chc} - \chi_{ins} - \alpha_{ps} \frac{\rho_0}{\rho_{ps}} \right) + \\
 &+ \frac{\chi^{m_3+1}_{ins} K_3(T)}{1 + \frac{b_3\mu_{B_3}}{c_3\mu_{C_3}}} \quad (7)
 \end{aligned}$$

The equation for the volume fraction of intermediate substances:

$$\begin{aligned}
 -u \frac{d\chi_{ins}}{dy_1} &= \frac{(1-\beta)^{m_2} K_2(T)}{1 + \frac{b_2\mu_{B_2}}{c_2\mu_{C_2}}} \left(1 - \psi - \chi_{chc} - \chi_{ins} - \alpha_{ps} \frac{\rho_0}{\rho_{ps}} \right) - \\
 &- \chi^{m_3+1}_{ins} K_3(T) \quad (8)
 \end{aligned}$$

where $K_i(T) = k_i e^{\left(\frac{E_i}{RT}\right)}$ -Arrhenius's function .

Hence nine differential equations are received , these equations contain ten unknowns :

$$\alpha_{i(i=1:4)}, \rho_g, v_g, P, T, \chi_{chc}, \chi_{ins}, \psi$$

The Clapeyron - Mendeleev equation can be used to close the system of equations.

$$P = \rho_g RT \quad (9)$$

As a result the system is received which describes the chemical processes proceeding in the pyrolysis zone .

For the integration of equations it is necessary to write boundary conditions , some of which refer to the material surface -

$$P_s = P = P_{ou}$$

$$q_s = \lambda_m \frac{dT_s}{dy} + a(T_\infty - T_s) + u\rho_s(1 - \psi_s) + \chi_{inss} \left(\sum_{i=1}^4 Q_i m_{ic} - \rho_{ins} uH \right) + (1 - \psi_s) u T_s (\rho c)_m$$

$$\lambda_m = \lambda_g \psi_s + \lambda_{ins} \chi_{inss} + \lambda_{ps} \alpha_{ps} \frac{\rho_o}{\rho_{ps}}$$

$$(\rho c)_m (1 - \psi_s) = (\rho c)_{ins} \chi_{ins} + (\rho c)_{ps} \alpha_{ps} \frac{\rho_o}{\rho_{ps}}$$

and others - to the material volume

$$v_g = \alpha_i = \chi_{chc} = \chi_{ins} = 0 \quad , \quad i = 1:3$$

$$\begin{aligned} -\lambda_m \frac{dT}{dy_1} \Big|_{y_1=y_{lr}} &= -\Delta Q (1 - \psi_{in}) \rho_o u - u P_{tr} \psi_{tr} - u \psi_{in} \rho_{in} c_{vin} T_{in} + \\ &+ (1 - \psi_{in}) (\rho c)_m T_{in} u + \rho_{tr} c_{tr} (1 - \psi_{tr}) T_{tr} u + \\ &+ \rho_g^{tr} \psi_{in} u H \end{aligned} \quad (10)$$

They hold true for coordinate $y_1 = y_{lr}$. In other words the above problem is a boundary problem .

We have solved the equations (2) - (9) by the Runge - Cutta method of the fourth order of accuracy . Simultaneously the Cauchy problem was solved . Equations were intergrated from the inside of the material to its surface . The

pressure was taken at $y_1 = y_{1tr}$ and y_{1tr} . For the verification of arbitrary taken values boundary conditions were investigated on the material surface regarding P_{1tr} and y_{1tr} as implicit functions P_s and q_s .

The corresponding relations between P_{1tr} and y_{1tr} as functions P_s and q_s were determined by the Newton modified method. The ablation rate u as the first approximation was taken on the basis of qualitative observations and hence is redetermined in accordance with the formula (1).

As a result of calculations the qualitative pattern of changing the active component fraction β and the intermediate substance fraction χ_{ins} was obtained (fig. 2)

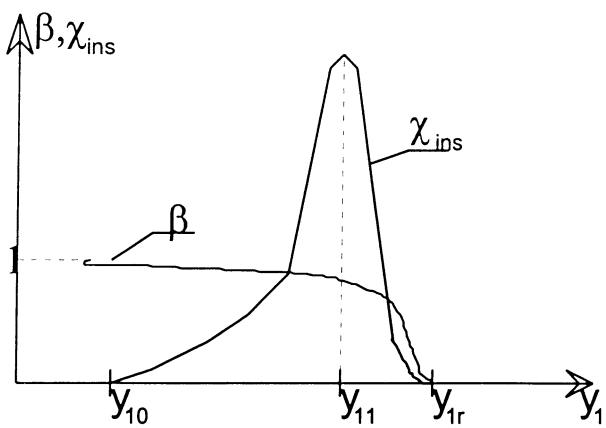


Fig . 2 . The qualitative pattern of the active component fraction - β and of the intermediate substance fraction - χ_{ins} .

The solution of the problem (fig. 2) confirms the tendency of proceeding the polyacrylonitrile pyrolysis process .

References .

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