MODELLING OF PYROLYSIS PROCESSES OF POLYACRYLONITRILE

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ABSTRACT

The modelling of carbon substances obtaining, for instance, carbon fibers which have high fire resistance, has been realized on the example of the polyacrylonitrile pyrolysis modelling. The pyrolysis is considered as a double step process when the formation of a liquid phase and the oxidation of substance are excluded. Three main reactions are considered: a) with the evolution of ammonia; b) with the evolution of hydrogen cyanide; c) with the evolution of hydrogen. Reactions b) and c) are sequential, and 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 kinetic characteristics of the above reactions and the thermodynamic parameters of reagents and products in these reactions. The equations received are calculated by Runge-Cutta method and by Adams method of the fourth order accuracy.

Equally to above mentioned mathematical model, in accordance with semiempirical methods of quantum chemistry, the computing modelling of ammonia and hydrogen cyanide evolution from model system simulating polyacrylonitrile chain link has been carried out. The possibility of these processes proceeding and also the favourable way of ammonia and carbon substances formation has been established.

INTRODUCTION

The polyacrylonitrile(PAN) is one of the main types of substances used for the production of carbon fibres. The structure of this polymer and its intermediates promotes to carbon fibres formation by the pyrolysis[1]. In our case 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) destructs with the formation of a solid residue (carbon material or coke), gaseous substances and intermediate solid substances. Here the investigation of intermediate substance resistance by the semiempirical methods of quantum chemistry can be interesting for the destruction theory development. The PAN pyrolysis processes which proceed at 673-1073 K are considered. At these temperatures three main consequential-parallel reactions of a polymer thermodestruction take place, and besides intermediate solid substances which participate in the creation of a fiber carbon structure or carbon tubes are formed.

DESCRIPTION OF PHYSICO-CHEMICAL PROCESSES DURING THE
POLYACRYLONITRILE PYROLYSIS

It is known[1] that the polyacrylonitrile powder heated to $T = T_{1c} = 523K$ is transformed into the cyclic polymer. As a result the material becomes more compact than the initial polymer. The cyclization process is accompanied by the heat emitting, the thermal conductivity increasing and also by the changing of material properties such as density and heat capacity. These processes inside the material are taken into account when $y_1 = y_{1c}$ and $T = = T_{1c}$.

Thus we should consider four chemical processes: a) the cyclization of PAN molecules; b) the destruction with the evolution of ammonia; c) the destruction with the evolution of hydrogen cyanide and with the formation of intermediate substances - polyenes; d) the destruction of polyenes with the evolution of hydrogen (reaction schemes are given in Fig.1).

The temperature of the beginning of the second reaction (b in Fig.1) is 673K. This reaction proceeds with the destruction of the initial substance and is accompanied by the carbonization. At the same time the third reaction begins at 723K with the formation of a polyene (intermediate substance) which is active in the carbonization with the evolution of hydrogen (the fourth reaction) that starts at 823K. Gases formed in the material volume are filtered through the material pores to its surface and enter into the environment.

Simultaneously oxidizers are diffused from the surroundings to the material surface. Such oxidizers as Oxygen, Water and Carbon Oxide interact with the carbon net formed during the polyacrylonitrile pyrolysis (the scheme of these reactions is given in Fig.2).

The rate of these reactions promotes the carbon layer decrease between the material surface and the coordinate y_1 equaled to y_{10}. This decrease is small. Therefore let us assume the thickness of the following layer in the material volume at stationary conditions.

DESINING OF THE MATHEMATICAL MODEL

The mathematical model of the polyacrylonitrile pyrolysis under the above assumptions is designed using the data of physico-chemical processes [2]. The problem of PAN pyrolysis can be conditionally divided in four subproblems for the following processes: a) processes proceeding on the material surface; b) processes of cyclization at $y_1 = y_{1c} - y_{1d}$; c) processes of PAN destruction at $y_1 = y_{1d} - y_{10}$; d) finishing processes at $y_1 = y_{10}$ corresponding to carbon substances formation.

For processes which flow on the material surface the system of two nonlinear equation is solved:

$$\Delta q_s = \Delta q_s(y_{1c}, P_c) \qquad (1)$$

$$P_s = P_s (y_{1c}, P_c) \qquad (2)$$

Then the rate of products evolution from material is calculated:

$$u = f(\rho_{chc}, m_{is}) \qquad (3)$$

For the zone of cyclization reactions the system of the following equations is solved:

equation of impulses

$$v'_g = f_{vg}(v_g, \beta', P') \qquad (4)$$

equation of heat flow

$$(dT/ dy_1) = f_3 (P, \lambda_m, c_v, \rho_g, u, H, T, \Delta Q) \qquad (5)$$

contiuity equation

$$(d\rho_g/dy_1) = f_1(\psi, \rho_g, u, v_g, m_{ig\ i=1...3}, v'_g, \psi') \qquad (6)$$

Clapeyron-Mendeleev equation

$$P = f_{10}(\rho_g, R(\alpha_i), T) \qquad (7)$$

Chemical reactions 2, 3, 4 flow in the destruction zone. These reactions can be describe by the geometric relations and conservation laws[3,4]. As a result the system of the following equations are received:

continuity equation

$$d\rho_g/dy_1 = f_1(\psi, \rho_g, u, v_g, m_{ig\ i=1...3}, v'_g, \psi') \qquad (8)$$

concentration equation

$$d\alpha_i/dy_1 = f_j(\psi, \rho_g, u, v_g, m_{ig}, v'_g, \psi', \rho'_g, \alpha_i) \qquad (9)$$

$$j = 2...4, \quad i = 1...3$$

impulse conservation equation

$$dv_g/dy_1 = f_5(\psi, \rho_g, u, v_g, \psi', \rho'_g, \tau, P') \qquad (10)$$

porosity equation

$$d\psi/dy_1 = f_6(\psi, u, \beta, K_i(T)_{i=1...3}, \chi_{ins}, \chi_{chc}) \qquad (11)$$

equation of the volume fraction of changing coke

$$d\chi_{chc}/dy_1 = f_7(u, \beta, K_i(T)_{i=1...3}, \psi, \chi_{ins}, \chi_{chc}) \qquad (12)$$

equation of the volume fraction of intermediate substances

$$d\chi_{ins}/dy_1 = f_8(\psi, u, \beta, K_i(T)_{i=1...3}, \chi_{chc}, \chi_{ins}) \qquad (13)$$

energy conservation equation

$$d\lambda_m/dy_1 * dT/dy_1 = f_9(\psi, \rho_g, u, v_g, m_{ig\ i=1...3}, v'_g, \rho'_g, \psi', H$$
$$E, T, Q_{i\ i=1...3}, T', E', H') \qquad (14)$$

Clapeyron-Mendeleev equation

$$P = f_{10}(\rho_g, R(\alpha_i), T) \qquad (15)$$

For the finishing stage this system of equations as well as for the zone of cyclization processes is solved but in this case the calculations are made with other initial conditions.

Thus for the solution of problem we propose 10 equations based on the conservation laws, relations of heat conductivity, Clapeyron-Mendeleev and also based on Arrhenius's function. For the integration of equation received the boundary conditions some of which refer to the material surface

and others - to the material volume had been written. On the surface of PAN we have solved the problem by Newton modified method, and in the volume Runge-Cutta method and Adams method were used.

INVESTIGATION OF CHEMICAL PARTICLES STABILITY BY SEMIEMPIRICAL METHODS OF QUANTUM CHEMISTRY

On the base of program product "Hyperchem" and semiempirical methods of quantum chemistry we have investigated different ways of chemical reactions between the groups of reagents simulating chains of polyacrylonitrile (PAN) and their transformations during the polyacrylonitrile destruction process. Modelling was made by molecular dynamics method at the temperature 700 K during 1 Ps. After that we optimized the products geometries by steepest descent method. The total energy and gradient were calculated using PM3 method.

We considered three models of PAN pyrolysis. In the first case considered system was modelled by two molecules of ethylcyanide in molecular hydrogen environment added to imitate the presence of segments of other PAN molecules. Initially the reagents were situated optimally for reaction proceeding. As a result formation of carbon ring took place with evolution of ammonia or cyanide depending on initial conditions. In the second case the reaction between 1 amino 2,4 dimethyl cyclopentylimine and propane was considered. The initial location and velocity of propane were imposed to "push out" the nitrogen atom from the ring. At the corresponding initial conditions the carbon ring and ammonia were obtained. Sometimes there was a carbon bridge between ring atoms. In the third case we considered interaction between tetracyanononane and decane placed parallelly and optimally to form carbon rings during reaction. Here we obtained irregular ring structures of different numbers of atoms including nitrogen; in this case ammonia was not evoluted.

In dependence on the initial rates and mutual disposition of reagents corresponding to the temperature and pressure in real process different ways of reaction are possible. It is impossible to find statistical relationships of this process, but we have observed some characteristic ways of reactions such as formation of carbon rings with parallel release of molecular hydrogen, hydrogen cyanide and ammonia. In the same time the possibility of intermediate products formation with amine, imine, cycloaliphatic and aromatic groups occurs. The preferred releasing of ammonia (or nitrogen from ring) proceeds to carbon containing cycles formation.

NUMERICAL EXPERIMENT FOR THE DETERMINATION OF PROCESS PARAMETERS

The system of differential equations is led to convenient mode of programming. The functional scheme of program product is created and the examination of mathematical model has been carried out. The numerical experiment allowed to receive the differential patterns of carbon substances formation as well as gaseous substances evolution during the changing of initial parameters and conditions of processes. In program operation the dependence of volume fraction of changing coke (carbon substances) and gas concentration dependence upon the temperature are obtained. Some results concerning the ammonia evolution and the polyene (intermediate substance) formation in the dependence on the conditions of polyacrylonitrile pyrolysis are given in Fig. 3. From the data of Fig.3 it is seen that with the increasing of ammonia evolution the intermediate substance decreases, and the carbon output in the residue of pyrolysis increases, relatively. These dependences prove theoretical suppositions.

CONCLUSION

On the basis of the results obtained we can conclude: a) when the material warm-up is slower, the reaction with ammonia evolution and large coke output formation prevails;
b) when the material (PAN) warm-up is faster (the rate of process is higher by an order) the proceeding of two reactions (b and c reactions) leads to the carbon output decreasing.

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NOMENCLATURE

a - heat transfer coefficient; C_p, C_v - isobaric and isochoric heat capacities; E' - energy chan-

ging rate; E_{act} - activation energy; H -enthalpy; H'- enthalpy changing rate; K_i (T)-Arrhenius's function; m - mass; m_{ig} - mass fraction of i-gas; m_{is} - mass rate of the heterogeneous interactions of carbon with i-oxidizer (i = 1, 2, 3, 4) corresponding to area unit of material surface; P - pressure; P'- pressure changing rate; P_c - pressure on the cyclization stage; P_s - function of pressure changing on the material surface; Q_i - heat removal on the chemical reaction proceeding; Δq_s - function of the heat changing on the material surface induced by the chemical reactions proceeding; R - function depending on the i-gas concentration; t - time; T-temperature; T'- temperature changing rate; u - material decomposition rate; W - volume; y - - space coordinate; y_{lc} - coordinate of cyclization reaction; α - mass concentration; α_i - gas concentration; β - volume fraction of the destructive component; λ - thermal conductivity; v-process rate; v_g- gas velocity; v_g'- derivative of gas velocity; ρ - density; ρ_{exc} - density of changing coke; ρ_g - gas density; τ - friction function; χ_{ins} - volume fraction of intermediate substances; χ_{exc} - volume fraction of changing coke during the pyrolysis; χ_{ps} - volume fraction of initial passive substances (in our case, this value tends to zero); ψ'- porosity changing rate; ψ - the porosity.

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FIGURES

a) $-CH_2\ CHCH_2\ CH- \longrightarrow -CH_2CHCH_2CH-$

$\quad\quad\ \ CN\quad\quad CN\quad\quad\quad\quad\quad = N-\ C= N-\ C=N-\ ;$

b) $-[-C_3H_3N-]_n - \longrightarrow nNH_3\ +\ -[-C-]_{n1}-\ ;\ n_1 = 3n;$

c) $-[-C_3H_3N-]_n- \longrightarrow nHCN\ +\ -[-CH=CH-]_n-\ ;$

d) $-[-CH=CH-]_n- \longrightarrow nH_2\ +\ -[-C-]_{n2}-\ ;\ n_2 = 2n.$

Fig. 1. Some chemical equations of polyacrylonitrile pyrolysis process

a -cyclization of PAN, b - destruction of PAN (cyclic product) with

the ammonia evolution, c - destruction of PAN with the polyene

formation, d - destruction of polyene.

e) $C + H_2O \longrightarrow CO + H_2$

f) $C\ +\ CO_2 \longrightarrow 2CO$

g) $2C\ +\ O_2 \longrightarrow 2CO$

h) $C\ +\ O_2 \longrightarrow CO_2$

Fig. 2. Some Red-Ox reactions on the PAN surface with the inlet of an oxygen

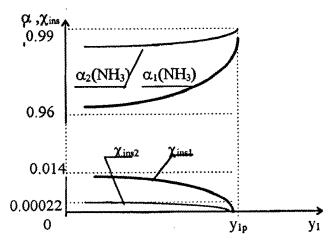containing chemical particles (e - water, f - carbon dioxide, g and h - oxygen)

Fig. 3. The changes of ammonia evolution and of polyene (intermedi-

ate substance) formation in the dependence on the transforma-

tion rate ($u_1 = 10^{-5}$, and $u_2 = 10^{-6}$)