Journal of Engineering Physics and Thermophysics, Vol. 76, No. 6, 2003

NUMERICAL CALCULATION OF VAPOR THERMOLYSIS OF ORGANIC WASTES

G. I. Zhuravskii and V. A. Sychevskii

UDC 536.246.2;519.6

Mathematical modeling and numerical calculation of thermolysis of organic materials were conducted in the medium of superheated vapor by an example of rubber.

The use of wastes in industry is an urgent problem. At present, combustion is the main method of their utilization. However, this is economically wasteful and ecologically harmful. An alternative method of reprocessing of wastes is thermolysis in the medium of inert gas.

In [1], thermal methods of reprocessing of biomass, rubber, and plastic wastes in the medium of superheated vapor are considered. This method offers promise since it reduces to minimum the danger of explosion and discharge of harmful substances to the surrounding medium.

The process of treatment of organic wastes by superheated vapor passes through several stages. At the first stage, the surface of the material is heated by superheated vapor to a certain initial temperature. Till the surface temperature is below the dew point, vapor condenses on it. This causes intense heating of the surface at the expense of the energy of phase conversion. The condensing vapor forms a liquid film on the surface, which fills the pores between the particles and is absorbed by the porous space of the particles themselves. At the second stage, water evaporates from the material, which impedes the process of material heating since a portion of energy is spent for evaporation. The stage terminates with complete evaporation of moisture. The third stage is characterized by heating of the material without phase conversions and chemical reactions. It ceases when the surface reaches a temperature T_d. The fourth stage begins with destruction of the solid phase. Not the entire solid phase, but only a part of it (mainly the binder) is destroyed. This stage results in thermal decomposition of the material.

Processing of the material (e.g., worn rubber tires) as a whole has its advantages, since the stage of preliminary comminution of the material is eliminated, which allows one to reduce energy consumption. However, in a number of cases this leads to a decrease in the efficiency of equipment due to ineffective use of the reaction space. Therefore, to improve the efficiency of pyrolysis systems, wastes are precomminuted. We consider both variants.

We consider the problem of thermolysis of rubber tires as a whole. Rubber tires having a temperature of $T_0 = 20^oC$ are loaded (one over another, thus forming a cylinder) into the reactor with a height $H = 2$ m and a base area $S = 1\ m^2$. Superheated vapor with a temperature $T_\infty = 500^oC$ and density $\rho_v = 0.322\ kg/m^3$ is supplied from below to this structure at a velocity $v_v = 0.1$ m/sec. The vapor heats the rubber to $T_d = 400^oC$, the heat of rubber thermodestruction $Q_d = 600$ kJ/kg, and the heat of evaporation of liquid products $Q_{ev} = 300$ kJ/kg. In decomposition of rubber, 40% of its initial mass is removed by water vapor in the form of gas. Then, the vapor-gas mixture is separated by cooling into the liquid fraction and gas fuel, which is used to maintain the process of thermolysis. The remainder is solid carbon.

The estimates made [2] showed that under the conditions considered the flow is laminar. Therefore, we assume that the flow follows the contours of the tire surface. In this case, the complex inner surface of the tire can be substituted by a smooth cylindrical surface. Here, the effective thickness of the cylinder wall is taken to be 0.013 m and the outer radius $R_{out} = 0.55$ m.

The coefficients of mass transfer of vapor β_v and the products of decomposition of rubber wastes β_g which were obtained in [2] are $3.87 \cdot 10^{-8}$ kg/(m^2·sec·Pa) and $2.0 \cdot 10^{-4}$ m/sec, respectively. The concentration of gaseous products of decomposition near the phase interface is $C_s = 3.62\ kg/m^3$.

A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 6, pp. 104–109, November–December, 2003. Original article submitted March 6, 2003.

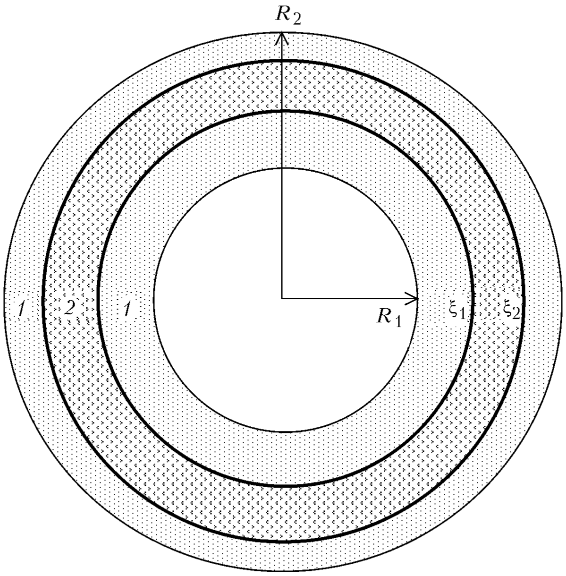

Fig. 1. Geometric scheme of the problem of thermal decomposition of rubber tires in the form of a cylinder.

Let heat fluxes at the ends of the hollow cylinder be zero and heat fluxes through inner and outer side surfaces be independent of coordinates; then the temperature changes only along the radius. The geometric scheme of the problem is given in Fig. 1. Here, 1 is the carbon remainder and 2 is the initial tire. Since the cylinder is heated from both inner and outer surfaces, two phase fronts, whose boundaries are determined as $\xi_1(\tau)$ and $\xi_2(\tau)$, exist in the wall. If the products evaporate from the outer surfaces, then $Q_{\text{ph}} = Q_{\text{d}}$, and evaporation is taken into account in the corresponding boundary conditions. If evaporation occurs on the front of phase transition inside the material, then $Q_{\text{ph}} = Q_{\text{d}} + Q_{\text{ev}}$.

At the first stage, when water vapor condenses (or evaporates) on the surface, we have

$$(c\rho)_{\text{t}} \frac{\partial T_2}{\partial \tau} = \operatorname{div} (\lambda_{\text{t}} \operatorname{grad} T_2) \tag{1}$$

and the boundary conditions are

$$\lambda_{\text{t}} \operatorname{grad} T_1 \big|_{R_1,R_2} = \alpha (T_\infty - T_{\text{s}}) + Q_{\text{w}} \beta_{\text{v}} (P_\infty - P_{\text{v}}) . \tag{2}$$

When all water evaporates from the surface, Eq. (1) remains the same and the boundary conditions take on the form

$$\lambda_{\text{t}} \operatorname{grad} T_1 \big|_{R_1,R_2} = \alpha (T_\infty - T_{\text{s}}) . \tag{3}$$

When the surface reaches the temperature of destruction, the system of differential equations is written as

$$(c\rho)_{\text{c}} \frac{\partial T_1}{\partial \tau} = \operatorname{div} (\lambda_{\text{c}} \operatorname{grad} T_1) , \quad R_1 < r < \xi_1 (\tau) \quad \text{and} \quad \xi_2 (\tau) < r < R_2 ; \tag{4}$$

$$(c\rho)_{\text{t}} \frac{\partial T_2}{\partial \tau} = \operatorname{div} (\lambda_{\text{t}} \operatorname{grad} T_2) , \quad \xi_1 (\tau) < r < \xi_2 (\tau) , \tag{5}$$

and evaporation on the surfaces must be taken into account:

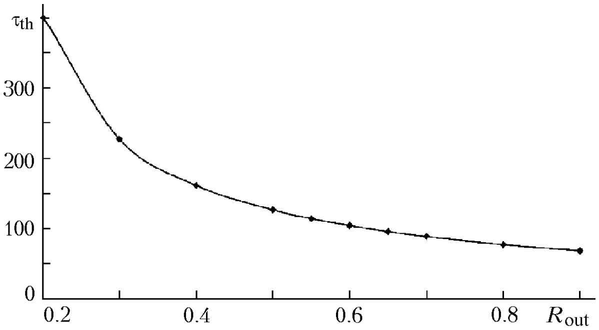

Fig. 2. Dependence of the time of thermolysis τ_{th} on the outer radius of the tube R_{out}. τ_{th}, min.

$$\lambda_c \operatorname{grad} T_1 \big|_{R_1,R_2} = \alpha\,(T_\infty - T_s) + Q_{ev}\,\beta_g\,(C_s - C_\infty)\,. \tag{6}$$

On the boundaries of phase transitions we have

$$-\lambda_c \operatorname{grad} T_1 \big|_{\xi_1} + \lambda_t \operatorname{grad} T_2 \big|_{\xi_1} = \rho_t Q_{ph} \frac{\partial \xi_1}{\partial \tau}\,, \quad T_1 \big|_{\xi_1} = T_2 \big|_{\xi_1} = T_d\,; \tag{7}$$

$$-\lambda_t \operatorname{grad} T_2 \big|_{\xi_2} + \lambda_c \operatorname{grad} T_1 \big|_{\xi_2} = \rho_t Q_{ph} \frac{\partial \xi_2}{\partial \tau}\,, \quad T_1 \big|_{\xi_2} = T_2 \big|_{\xi_2} = T_d\,. \tag{8}$$

To calculate vapor flow we must know the pressure of saturated vapor of water near the surface P_v. To do this we use the formula

$$P_v = 2\cdot 10^4 \exp\left(15.3\cdot\frac{T - 333}{T}\right). \tag{9}$$

A control-volume approach was used for solution of the problem formulated. The difference scheme was calculated by the marching technique. The algorithm constructed allows solution of the problem with several simultaneously existing fronts of phase transition since the cylinder is washed by superheated vapor from both inside and outside. In this case, we took into account the following phase transitions: water–vapor and gas–liquid products of decomposition–solid material.

The following supplementary data were used in the calculations: ρ_t = 1120 kg/m^3, c_t = 1830 J/(kg·K), λ_t = 0.15 W/(m·K), ρ_c = 1650 kg/m^3, c_c = 692 J/(kg·K), λ_c = 0.17 W/(m·K), and α = 8 W/(m^2·K).

As a result of the calculations we obtained:

1. *Initial heating of tires from the surrounding temperature to 100^{o}C.* In this case, heating occurs due to heat transfer and heat of the phase transition. The maximum heat flux which forms as a result of phase transition in condensation is equal to q_v = 8903 W/m^2; the same due to convective heat transfer is q = 3727 W/m^2. The mass of condensed vapor is m_v = 920 g. The length of this stage is τ_{st} = 2 min, and the amount of consumed energy is Q = 7.5 MJ.

2. *Heating of tires from 100^{o}C to the temperature of their destruction, 400^{o}C.* Heating takes place only due to heat transfer. The maximum heat flux is q = 3176 W/m^2. The length of the stage is τ_{st} = 42.5 min. The amount of energy spent for heating is Q = 59.7 MJ.

3. *Destruction of rubber and its evaporation.* At this stage, the maximum heat flux due to heat transfer is q = 801 W/m^2; the same due to evaporation of rubber is q_g = –217 W/m^2. The time spent for destruction is τ_{st} = 63 min. The amount of consumed energy is Q = 37.6 MJ.

Figure 2 presents the dependence of the time of rubber thermolysis at α = 8 W/(m^2·K) on the outer radius of the tube R_{out}. As the radius increases the time of thermolysis decreases, and, consequently, with an increase in the surface area of tires under pyrolysis the time of their destruction decreases; therefore, other conditions being equal, the

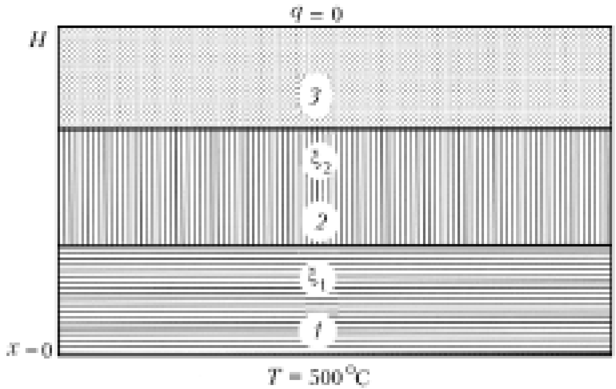

Fig. 3. Geometric scheme of the problem of thermal decomposition of crushed rubber wastes.

rate of thermolysis is higher in those packings of rubber tires where the surface area washed by the vapor-gas medium is larger.

Further, we consider the process of thermal decomposition of crushed rubber wastes in the medium of superheated water vapor blown through the layer of wastes. We assume that the reactor, into which wastes are supplied, has the same dimensions H and S as in the first case. Figure 3 shows the geometric scheme of the problem. Zone 1 is the filling of solid products of decomposition (carbon particles), 2 is the zone of rubber particles at a temperature higher than 100°C (therefore, water–vapor phase transitions are absent in it), 3 represents the particles with water condensed on them, ξ_1 is the boundary of the phase transition "rubber–gaseous products of decomposition," and ξ_2 is the boundary of the phase transition "water–vapor."

Moving through the porous filling, superheated water vapor carries heat, the amount of which (liberated in the volume unit per time unit) is determined by the expression [3]

$$Q_v = -\,Q_{\text{w}}\,\mathbf{v}\;\text{grad}\;\rho_{\text{sat}} - \rho_{\text{sat}}\,\mathbf{v}\,c_{\text{v}}\;\text{grad}\;T\,. \tag{10}$$

The first term on the right-hand side of Eq. (10) reflects heat transfer due to phase transition related to condensation of water, and the second term — to convective heat transfer.

With the fact that heat conduction is characterized by the term div ($\lambda_{\text{ef}}(T)$ grad T), the equation of heat transfer in the layer of wastes can be presented in the form

$$[(1-\varepsilon)\,(c\rho)_{\text{t}} + \varepsilon\,(c\rho)_{\text{v}}]\,\frac{\partial T}{\partial \tau} = \text{div}\,(\lambda_{\text{c,ef}}\;\text{grad}\;T) - \frac{c_{\text{v}}\,\rho_{\text{sat}}\,\mathbf{v}}{\varepsilon}\;\text{grad}\;T - \frac{Q_{\text{w}}\,\mathbf{v}}{\varepsilon}\;\text{grad}\;\rho_{\text{sat}}\,. \tag{11}$$

In the initial period, when the filling is heated to a temperature of 100°C, we use Eq. (11) with the following boundary conditions:

$$T_2\big|_{\xi_2} = T_3\big|_{\xi_2} = T_{\text{w}}\,,\quad T\big|_{x=0} = 500^{\circ}\text{C}\,,\quad q\big|_{x=H} = 0\,. \tag{12}$$

It is assumed that there are no heat fluxes through the side surfaces. These boundary conditions are retained during the entire process of thermolysis.

When water evaporates from the surfaces of the particles in the filling, we have

$$[(1-\varepsilon)\,(c\rho)_{\text{t}} + \varepsilon\,(c\rho)_{\text{v}}]\,\frac{\partial T_2}{\partial \tau} = \text{div}\,(\lambda_{\text{c,ef}}\;\text{grad}\;T_2) - \frac{c_{\text{v}}\,\rho_{\text{sat}}\,\mathbf{v}}{\varepsilon}\;\text{grad}\;T_2\,. \tag{13}$$

On the boundary of the phase transition we write

$$\lambda_{\text{t,ef}}\frac{\partial T_3}{\partial x}-\lambda_{\text{t,ef}}\frac{\partial T_2}{\partial x}-(\rho v c)_{\text{v}}\,(T_3\,(M+\Delta h)-T_2\,(M-\Delta h))=\nu_{\text{w}}\varepsilon\rho_{\text{w}}Q_{\text{w}}\frac{\partial \xi_2}{\partial \tau}\,,\quad T_2\big|_{\xi_2}=T_3\big|_{\xi_2}=T_{\text{w}}\,. \tag{14}$$

When the filling is heated above the temperature of destruction T_{d}, we must solve the following system:

$$[(1-\varepsilon)\,(c\rho)_{\text{c}}+\varepsilon\,(c\rho)_{\text{v}}]\,\frac{\partial T_1}{\partial \tau}=\text{div}\,(\lambda_{\text{c,ef}}\,\text{grad}\,T_1)-\frac{c_{\text{v}}\,\rho_{\text{sat}}\,\mathbf{v}}{\varepsilon}\,\text{grad}\,T_1\,,\quad 0<r<\xi_1\,(\tau)\,; \tag{15}$$

$$[(1-\varepsilon)\,(c\rho)_{\text{t}}+\varepsilon\,(c\rho)_{\text{v}}]\,\frac{\partial T_2}{\partial \tau}=\text{div}\,(\lambda_{\text{c,ef}}\,\text{grad}\,T_2)-\frac{c_{\text{v}}\,\rho_{\text{sat}}\,\mathbf{v}}{\varepsilon}\,\text{grad}\,T_2\,,\quad \xi_1\,(\tau)<r<\xi_2\,(\tau)\,; \tag{16}$$

$$[(1-\varepsilon)\,(c\rho)_{\text{t}}+\varepsilon\,(c\rho)_{\text{v}}]\,\frac{\partial T_3}{\partial \tau}=\text{div}\,(\lambda_{\text{c,ef}}\,\text{grad}\,T_3)-\frac{c_{\text{v}}\,\rho_{\text{sat}}\,\mathbf{v}}{\varepsilon}\,\text{grad}\,T_3-\frac{Q_{\text{w}}\,\mathbf{v}}{\varepsilon}\,\text{grad}\,\rho_{\text{sat}}\,,\quad \xi_2\,(\tau)<r<H\,. \tag{17}$$

On the boundary of the phase transition "rubber–gaseous products of decomposition" we have

$$\lambda_{\text{t,ef}}\frac{\partial T_2}{\partial x}-\lambda_{\text{c,ef}}\frac{\partial T_1}{\partial x}-(\rho v c)_{\text{v}}\,(T_2\,(M+\Delta h)-T_1\,(M-\Delta h))=\nu_{\text{t}}\,(1-\varepsilon)\,\rho_{\text{t}}Q_{\text{ph}}\frac{\partial \xi_1}{\partial \tau},\ T_1\big|_{\xi_1}=T_2\big|_{\xi_1}=T_{\text{d}}\,, \tag{18}$$

and on the water–vapor boundary — (14).

Assuming the filling to be isotropic and consisting of spherical particles, we can use the formulas

$$\frac{\lambda_{\text{c,ef}}}{\lambda_{\text{v}}}=1+\frac{3\,(1-\varepsilon)\,(\lambda_{\text{c}}/\lambda_{\text{v}}-1)}{3+\varepsilon\,(\lambda_{\text{c}}/\lambda_{\text{v}}-1)}\,,\quad \frac{\lambda_{\text{t,ef}}}{\lambda_{\text{v}}}=1+\frac{3\,(1-\varepsilon)\,(\lambda_{\text{t}}/\lambda_{\text{v}}-1)}{3+\varepsilon\,(\lambda_{\text{t}}/\lambda_{\text{v}}-1)}$$

for calculation of the effective thermal conductivity.

Having applied formula (9) to the pressure of vapor P_{v}, we find the density of the saturated vapor from the expression

$$\rho_{\text{sat}}=\frac{2\cdot 10^4\,\exp\left(15.3\cdot\frac{T-333}{T}\right)}{R\,(273+T)}\,. \tag{19}$$

For the calculations we used the finite-difference scheme obtained by a control-volume approach. The problem under consideration was solved on the basis of the locally one-dimensional scheme. In this case, the problem was split into spatial variables. The technique allowed simultaneous account for the phase transitions "rubber–gaseous products of decomposition" and "water–vapor." The algorithm and the program for calculation of thermolysis of crushed rubber in the medium of superheated vapor stem from this technique. The results obtained are shown in Fig. 4.

Figure 4a gives the characteristic temperature distribution in the filling for different instants of time in the presence of phase transitions "rubber–gas" and "water–vapor." The distribution of temperature is of a complex character. Two inflection points which correspond to phase transitions are seen on the curves. Figure 4b presents the characteristic temperature distribution in the filling in the presence of the rubber–gas phase transition. In this case, it was assumed that the vapor which is filtered through wastes does not condense in the material. Comparison of results of the calculation shown in Figs. 4a and b indicates the difference in the behavior of the temperature fields with time. Total times of the process of pyrolysis are also different. For the first case it is the longest (Fig. 4a), and it is smaller for the second case (Fig. 4b). In the first case, it is necessary to spend time and energy for heating the filling and for the phase transitions associated with evaporation of the condensate and decomposition of the rubber; in the second case, energy is spent up to the phase transition related to the decomposition of rubber. The difference in the dynamics of the temperature fields is observed at the first stage of heating (depicted in Fig. 4c and d). Figure 4c characterizes

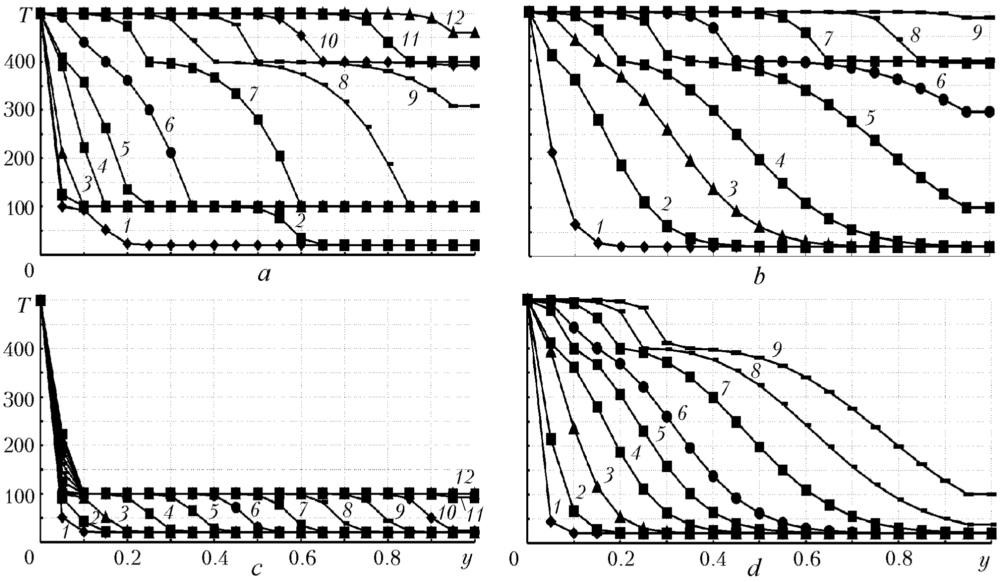

Fig. 4. Temperature distribution in the filling of rubber wastes as a function of time: in thermal decomposition and phase transitions "water–vapor" (a): 1) τ = 1; 2) 5; 3) 10; 4) 30; 5) 60; 6) 120; 7) 240; 8) 360; 9) 480; 10) 600; 11) 780; 12) 931 min; only in thermal decomposition (b): 1) τ = 10; 2) 60; 3) 120; 4) 180; 5) 300; 6) 420; 7) 600; 8) 780; 9) 960 min; in condensation of vapor (c): 1) τ = 0.17; 2) 0.5; 3) 1; 4) 2; 5) 3; 6) 4; 7) 5; 8) 6; 9) 7; 10) 8; 11) 9; 12) 10 min; in thermal decomposition during the initial period of time (d): 1) τ = 1; 2) 10; 3) 30; 4) 60; 5) 90; 6) 120; 7) 180; 8) 240; 9) 300 min.

the dynamics of temperature distribution in the filling in the presence of vapor condensation, whereas Fig. 4d shows the same in its absence. It is seen from Fig. 4c that during a small period of time (relative to the duration of the entire process) the temperature in the material reaches 100^{o}C. This is due to condensation of vapor in the volume.

It follows from the analysis of the results obtained that the dynamics of the development of the temperature field and of the field of moisture distribution are the same. This is confirmed by the fact that condensation of vapor is the main reason for heating of the filling to a temperature of 100^{o}C. Heating of the filling to a temperature of 100^{o}C in the absence of phase transitions follows another pattern. In this case, the main mechanisms of heating are heat conduction and convection, which lead to retarded heating of the filling. In the presence of the phase transition caused only by rubber decomposition, the filling is heated similarly to the latter case (Fig. 4d). The difference appears only when the temperature in the material reaches 400^{o}C (onset of rubber decomposition). Despite fast heating of the material to 100^{o}C due to condensation of vapor, further heating of it goes more slowly since energy is spent for both heating and phase transitions due to evaporation of water.

From the technological point view, the value of the temperature at the outlet from the reactor is of importance. At outlet temperatures of vapor below the dew point, condensation of vapor will take place, which is an undesirable effect. If the vapor temperature at the outlet is too high, the efficiency of heat exchange between the vapor and the material decreases. Optimum values of the vapor temperature are close to 300^{o}C. These are precisely the conditions under which it is possible for the products of decomposition of wastes to be removed from the reactor in the gaseous state. With this in view, we conducted numerical calculations of the dependence of the time of process termination τ_{fin} on the height of the filling H; in these calculations, the time when the upper layer of the filling was heated to a temperature $T = 300^{o}$C was taken as the time of process termination. Calculations were made for three values of the velocity of vapor supply v_{v} = 0.02, 0.05, and 0.1 m/sec.

Calculations made by the mathematical models suggested indicate the dynamics of the development of heat and mass transfer processes in thermolysis, which is in agreement with experimental data. The obtained values of the time of thermolysis, the time of moistening of wastes, and the amount of condensed vapor are in agreement with experimental data.

NOTATION

T, temperature, ^{o}C; T_w, temperature of phase transition "water–vapor," ^{o}C; T_d, temperature of material destruction, ^{o}C; H, reactor height, m; S, area of the reactor base, m^2; T_0, initial temperature, ^{o}C; T_∞, temperature of superheated vapor at the inlet to the reactor, ^{o}C; ρ_v, vapor density, kg/m^3; v_v, velocity of vapor, m/sec; Q_d, heat of rubber destruction, J/kg; Q_{ev}, heat of evaporation of liquid products of decomposition, J/kg; R_{out}, outer radius of a rubber tire, m; β_v, coefficient of mass transfer of vapor, kg/(m^2·sec·Pa); β_g, coefficient of mass transfer of gas, m/sec; C_s, gas concentration on the surface, kg/m^3; Q_{ph}, heat of phase transition, J/kg; τ, time, sec; ρ_t, density of rubber, kg/m^3; c_t, heat capacity of rubber, J/(kg·K); λ_t, thermal conductivity of rubber, W/(m·K); α, heat-transfer coefficient, W/(m^3·K); R_1 and R_2, radii of the inner and outer surfaces, m; Q_w, heat of evaporation (condensation) of water (vapor), J/kg; P_∞, pressure of vapor at a distance from the surface, Pa; P_v, pressure of saturated vapor of water near the surface, Pa; T_s, temperature of vapor-gas medium on the surface, K; ρ_c, density of carbon remainder, kg/m^3; c_c, heat capacity of carbon remainder, J/(kg·K); λ_c, thermal conductivity of carbon remainder, W/(m·K); r, radial coordinate, m; C_∞, gas concentration at a distance from the surface, kg/m^3; $\frac{\partial\xi}{\partial\tau}$, velocity of motion of the front of phase transition, m/sec; q, heat-flux density, W/m^2; τ_{st}, stage duration, sec; m_v, mass of condensed vapor, kg; Q, energy, J; Q_v, heat source, J; $\mathbf{v}$, vector of vapor velocity, m/sec; ε, porosity of the filling; ρ_{sat}, density of saturated vapor of water, kg/m^3; c_v, heat capacity of vapor, J/(kg·K); λ_{ef}, effective thermal conductivity of the filling, W/(m·K); x, coordinate along the height of the filling, m; Δh, small quantity of the length in the direction perpendicular to the surface of phase transition, m; $M = 2\Delta h$; R, gas constant, J/(kmole·K); λ_v, thermal conductivity of vapor, W/(m·K); ν_t, fraction of decomposed rubber; ν_w, fraction of water in the pores. Subscripts: 0, initial value; 1, 2, and 3, refer to materials in the corresponding zones of phase transitions; s, surface; st, stage; t, tire; th, thermolysis; w, water; ph, phase; b, boiling; fin, final; d, destruction; c, carbon remainder; v, vapor; out, outer; sat, saturated; g, gas; ev, evaporation; ef, effective.

REFERENCES

1. D. V. Aristarkhov, N. N. Egorov, G. I. Zhuravskii, É. P. Polesskii, and N. S. Sharanda, *Vapor Thermolysis of Organic Wastes* [in Russian], Minsk (2001).
2. G. I. Zhuravskii and V. A. Sychevskii, in: O. G. Martynenko (ed.), *Collection of Sci. Papers "Heat and Mass Transfer-2001"* [in Russian], Minsk (2002), pp. 13–20.
3. D. V. Aristarkhov and V. A. Sychevskii, *Vestsi Nats. Akad. Navuk Belarusi, Ser. Fiz.-Tékh. Navuk*, No. 1, 102–108 (2002).