# MATHEMATICAL MODEL OF THE THERMODESTRUCTION OF WORN TIRES IN OVERHEATED STEAM 

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A mathematical model of the heat and mass transfer in the process of thermolysis of rubber-technical articles in overheated steam is proposed.

Keywords: overheated steam, thermodestruction, tires, mathematical model, equations of interpenetrating continua.
Introduction. The problem of reclaiming and processing used tires is of great economic importance for the majority of developed countries. Several techniques for reclaiming tires [1-7] with simultaneous obtaining of organic fuel or fillers for various mixtures have been described. One effective way of processing organic wastes is their thermal destruction in overheated steam [8]. The experimental tests of the new thermal technologies of processing used tires have shown that the use of overheated steam as a heat-transfer medium and a transport medium for decomposition products is promising. These advantages are the possibilities of using condensation methods for concentrating decomposition products and reclaiming secondary heat preventing release into the atmosphere of decomposition products.

The processing consists of the fact that rubber heated in steam decomposes into two components: the gas component (volatile hydrocarbons) and the solid component (technical carbon with a metal cord). Volatile compounds neutralized by the steam enter the cooler and condense, forming a liquid hydrocarbon fraction corresponding to boiler oil [8-10].

In [11], a simple physical model was formulated and a calculation scheme based on the balance equations of such parameters as the temperature, the time of heating to a given temperature, and the geometric dimensions of the thermolysis reactor was proposed. A method of numerical calculation of the steam thermolysis of organic wastes was proposed in [12]. Analysis therewith is performed on the basis of the Stefan two-front one-dimensional problems in two variants: for one tire and for an isolated three-layer plate of comminuted wastes. Of interest is the investigation [13] in which conjugate turbulent heat and mass transfer at chemical transformations (polymerization processes) is considered.

In the present work, a mathematical model of thermolysis of worn tires in overheated steam based on the two-dimensional system of equations of interpenetrating continua [14] is proposed. The porosity is assumed constant by virtue of the fact that because of the presence of a metal cord pieces of rubber in general hold their shape in the process of thermolysis, only decreasing somewhat in volume.

At the initial instant of time the overheated steam hitting pieces of worn tires cools down and condenses. Due to the heat of overheating and phase transition the rubber is heated to a temperature above $T=100^{\circ} \mathrm{C}$, and the condensation process thereby ends. The stage of evaporation of the condensate ensues. Upon complete evaporation of the condensate the material is heated further to a temperature at which thermal destruction of the rubber begins. It has been found experimentally that destruction of the rubber occurs with the formation at the initial instant of time of the liquid phase (the rubber surface is covered with drops of destruction products), which partly evaporates and partly undergoes secondary destruction with the formation of gaseous products [8]. It has been established that thermal destruction of the rubber begins at $T=280-300^{\circ} \mathrm{C}$ and ends at $T=450-500^{\circ} \mathrm{C}$ and proceeds with heat absorption.

According to the above-described basic physical concepts, let us formulate the system of mass balance, momentum, and energy equations for the reactor in which thermal destruction of worn tires occurs.

Let us formulate the statement of the problem.
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Mass Balance Equations. The pore space is partly occupied by the gas and partly by the steam, and the volume ratio is defined as the porosity $\varepsilon=V_{\mathrm{g}} / V$.

Let the gas consists of the set of $n+1$ gas components. The mass balance equation of the $i$ th component of the steam-gas mixture is

$$
\begin{equation*}
\varepsilon \frac{\partial\left(\rho_{\mathrm{g}} Y_{i}\right)}{\partial \tau}+\nabla \cdot\left(\rho_{\mathrm{g}} Y_{i} \mathbf{w}\right)=J_{\mathrm{t} i}+\varepsilon \nabla \cdot\left(\rho_{\mathrm{g}} D \nabla Y_{i}\right), \quad i=1, \ldots, n, \mathrm{e} \tag{1}
\end{equation*}
$$

where $n$ is the number of mixture components except for the steam; $\rho_{\mathrm{g}}=M_{\mathrm{g}} / V_{\mathrm{g}}$ is the true density of the mixture; $\rho_{i}=M_{i} / V_{\mathrm{g}}=\rho_{\mathrm{g}} Y_{i}$ is the true density of the $i$ th component of the mixture; $Y_{i}=\rho_{i} / \rho_{\mathrm{g}}$ is the mass concentration of the components; $D$ is the single diffusion coefficient for all mixture components; $J_{\mathrm{t} i}$ is the source of the $i$ th component of the mixture as a result of the chemical reaction or evaporation from the porous solid.

The expressions $\varepsilon \rho_{\mathrm{g}}$ and $\varepsilon \rho_{\mathrm{g}} Y_{i}$ are, respectively, the densities of the gaseous mixture and its components in the reactor volume:

$$
\varepsilon \rho_{\mathrm{g}}=\frac{V_{\mathrm{g}}}{V} \frac{M_{\mathrm{g}}}{V_{\mathrm{g}}}=\frac{M_{\mathrm{g}}}{V}, \varepsilon \rho_{\mathrm{g}} Y_{i}=\frac{M_{i}}{V}
$$

In particular, for $i=e$ (steam) expression (1) is written as

$$
\begin{equation*}
\varepsilon \frac{\partial\left(\rho_{\mathrm{g}} Y_{\mathrm{e}}\right)}{\partial \tau}+\nabla \cdot\left(\rho_{\mathrm{g}} Y_{\mathrm{e}} \mathbf{w}\right)=J_{\mathrm{t} . \mathrm{e}}+\varepsilon \nabla \cdot\left(\rho_{\mathrm{g}} D \nabla Y_{\mathrm{e}}\right) \tag{2}
\end{equation*}
$$

The source $J_{\text {t.e }}$ at condensation from the vapor phase to the liquid one on the surface of tires is negative, and at evaporation from the liquid phase to the vapor one it is positive. We write the expression for $J_{\text {t.e }}$ in the form

$$
\begin{equation*}
J_{\mathrm{t} . \mathrm{e}}=\varepsilon \frac{6(1-\varepsilon)}{d_{\mathrm{t}}^{2}} \operatorname{Sh} D\left[\rho_{\mathrm{e}, \mathrm{~s}}\left(T_{\mathrm{t} . \mathrm{g}}\right)-\rho_{\mathrm{e}}\right] \tag{3}
\end{equation*}
$$

Here $\mathrm{Sh}=d_{\mathrm{t}} \alpha_{M} / D$ is the Scherwood mass transfer number; $6(1-\varepsilon) / d_{\mathrm{t}}$ is the value of the specific surface of the solid per unit volume; $\alpha_{M}$ is the mass transfer coefficient, $\mathrm{m} / \mathrm{sec} ; \rho_{\mathrm{e}, \mathrm{s}}\left(T_{\mathrm{t} . \mathrm{g}}\right)$ is the temperature dependent density of saturated steam at a surface temperature $T_{\text {t.g }}$ (since the process proceeds at a constant pressure close to atmospheric, the pressure dependence of $\rho_{\mathrm{e}, \mathrm{s}}$ is neglected), $\rho_{\mathrm{e}}=\rho_{\mathrm{g}} Y_{\mathrm{e}}$ is the steam density.

The value of the Scherwood mass transfer number is calculated by the empirical dependence from [15]

$$
\begin{equation*}
\mathrm{Sh}=2+0.55 \mathrm{Re}_{\mathrm{t}}^{1 / 2} \mathrm{Sc}^{1 / 3} \tag{4}
\end{equation*}
$$

where $\operatorname{Re}_{\mathrm{t}}=\rho_{\mathrm{g}} w d_{\mathrm{t}} /\left(\mu_{\mathrm{g}} \varepsilon\right) ; \mathrm{Sc}=\mu_{\mathrm{g}} /\left(\rho_{\mathrm{g}} D\right)$. To determine the saturated steam density $\rho_{\mathrm{e}, \mathrm{s}}$, let us make use of the perfect gas equation

$$
\begin{equation*}
\rho_{\mathrm{e}, \mathrm{~s}}=\frac{P_{\mathrm{e}, \mathrm{~s}}}{R_{\mathrm{e}} T_{\mathrm{t} \cdot \mathrm{~g}}} \tag{5}
\end{equation*}
$$

The saturated steam pressure near the surface $P_{\mathrm{e}, \mathrm{s}}$ is given by the empirical formula for the saturation curve [14]

$$
\begin{equation*}
P_{\mathrm{e}, \mathrm{~s}}=\frac{P^{\prime}}{\exp \left(T^{\prime} / T_{\mathrm{t} . \mathrm{g}}\right)} \tag{6}
\end{equation*}
$$

where $T^{\prime}=4996 \mathrm{~K} ; P^{\prime}=6.4072 \cdot 10^{10} \mathrm{~Pa}$.
Write the equation of state of the multicomponent medium assuming the gas phase to be a perfect gas:

$$
\begin{equation*}
P=T_{\mathrm{g}} \rho_{\mathrm{g}} \sum_{i=1}^{n+1} Y_{i} R_{i}=T_{\mathrm{g}} \rho_{\mathrm{g}} \bar{R}, \tag{7}
\end{equation*}
$$

where $\bar{R}=\sum_{i=1}^{n+1} Y_{i} R_{i} ; R_{i}$ denotes the gas constants for a given component depending on its molecular weight.
Let us sum Eq. (1) over all values of $i$, and since $\sum_{i=1}^{n+1} Y_{i}=1$, we get the equation for the gaseous mixture density

$$
\begin{equation*}
\varepsilon \frac{\partial\left(\rho_{\mathrm{g}}\right)}{\partial \tau}+\nabla \cdot\left(\rho_{\mathrm{g}} \mathbf{w}\right)=\sum_{i=1}^{n+1} J_{\mathrm{t} i} \tag{8}
\end{equation*}
$$

Momentum Balance Equation. Write the equation of motion in the form of the Darcy law

$$
\begin{equation*}
\mathbf{w}=-\frac{K}{\mu_{\mathrm{g}}} \nabla P, \quad K=\frac{\varepsilon^{3}}{(1-\varepsilon)^{2}} \frac{d_{\mathrm{t}}^{2}}{150} . \tag{9}
\end{equation*}
$$

For highly permeable media, the Forchheimer equation with the quadratic term

$$
\begin{equation*}
-\nabla P=\frac{\mu_{\mathrm{g}}}{K} \mathbf{w}+\frac{\rho_{\mathrm{g}} a}{\sqrt{K}}|\mathbf{w}| \mathbf{w}, \quad a=\frac{1.75}{\sqrt{150}} \varepsilon^{3 / 2} \tag{10}
\end{equation*}
$$

is used.
Equation of Motion of the Porous Body Front. In the above equations, the porosity $\varepsilon$ was assumed constant everywhere. At the same time, the solid phase is expended in the process of thermolysis, which can be inconsistent with the constancy of $\varepsilon$. The assumption of constancy of $\varepsilon$ is justified by the fact that because of the metal cord rubber pieces in general hold their shape in the thermolysis process, only decreasing somewhat in volume, and this decrease is uniform with respect to their linear dimensions. Therefore, by virtue of such a decrease in dimensions, the packing density of pieces of tiers $\varepsilon$ is assumed constant, and account of the change in the volume in the given statement is realized by the fact that the porous layer height varies with time. It is believed that the porous layer remains flat and only descends. Over the porous body in the reactor there is a gas volume which increases. In the case of a constant density, the equation of the rate of change in the volume of the porous layer is of the form

$$
\begin{equation*}
(1-\varepsilon) \rho_{\mathrm{t}} \frac{\left|u_{\mathrm{t}}\right|}{z}=-J_{\mathrm{t}} . \tag{11}
\end{equation*}
$$

Here $u_{\mathrm{t}}=d z / d \tau$ is the velocity of motion of the porous body front; $J_{\mathrm{t}}=\sum_{i=1}^{n+1} J_{\mathrm{t} i}$ is the summed mass flow from the solid and liquid phases into the gas phase; $z$ is the coordinate along the reactor axis counted off from the entrance of vapor into the reactor.

It may be assumed for simplicity's sake that loosening of pieces of the material occurs at a constant volume $\left(u_{\mathrm{t}}=0\right)$, i.e., only the true density of the rubber changes with time according to the kinetic equation. Exactly such an assumption is used in the present paper.

Energy Equation. Let us write the thermal balance equation in the two-parameter approximation with two different temperatures $T_{\mathrm{t}}$ and $T_{\mathrm{g}}$. The average temperature of the solid body $T_{\mathrm{t}}$ varies as a result of the heat conduction, the interphase heat transfer, the heat $Q_{\mathrm{p}}$ expended in thermolysis, and the condensation (evaporation) heat $Q_{\mathrm{e}}$ :

$$
\begin{equation*}
(1-\varepsilon) \rho_{\mathrm{t}} C_{\mathrm{t}} \frac{\partial T_{\mathrm{t}}}{\partial \tau}=\nabla \cdot\left[\lambda_{\mathrm{t}}(1-\varepsilon) \nabla T_{\mathrm{t}}\right]-\alpha_{\mathrm{t} . \mathrm{g}}\left(T_{\mathrm{t}}-T_{\mathrm{g}}\right)+(1-\varepsilon) \frac{\partial \rho_{\mathrm{r}}}{\partial \tau} Q \cdot-Q_{\mathrm{e}} J_{\mathrm{t} . \mathrm{e}} \tag{12}
\end{equation*}
$$

Here $\rho_{\mathrm{g}}$ is the rubber mass in a unit volume of the tire.
Solid particles are not "temperature thin;" therefore, writing for the solid one temperature $T_{\mathrm{t}}$, we suppose that, firstly, thermal conditions exist, i.e., the rate of change in all local temperatures in the solid is approximately the same, and, secondly, the internal thermal resistance of a piece of rubber is included in the interphase heat transfer coefficient $\alpha_{t . g}$.

The gas phase temperature $T_{\mathrm{g}}$ varies as a result of the convective transfer, the heat conduction, and the interphase heat transfer

$$
\begin{equation*}
\varepsilon \rho_{\mathrm{g}} C_{\mathrm{g}} \frac{\partial T_{\mathrm{g}}}{\partial \tau}+\nabla \cdot\left[\rho_{\mathrm{g}} \mathbf{w} C_{\mathrm{g}} T_{\mathrm{g}}\right]=\nabla \cdot\left[\lambda_{\mathrm{g}, \mathrm{eff}} \varepsilon \nabla T_{\mathrm{g}}\right]+\alpha_{\mathrm{t} \cdot \mathrm{~g}}\left(T_{\mathrm{t}}-T_{\mathrm{g}}\right) \tag{13}
\end{equation*}
$$

here $\lambda_{\text {g.eff }}$ is calculated by the anisotropic dependence from $[16,17]$

$$
\left(\lambda_{\mathrm{g}, \mathrm{eff}}\right)_{\|}=\lambda_{\mathrm{g}}(\varepsilon+0.5 \mathrm{Pe}), \quad\left(\lambda_{\mathrm{g}, \mathrm{eff}}\right)_{\perp}=\lambda_{\mathrm{g}}(\varepsilon+0.1 \mathrm{Pe})
$$

where $\left(\lambda_{\mathrm{g} . \mathrm{eff}}\right)_{\|}$and $\left(\lambda_{\mathrm{g} . \mathrm{eff}}\right)_{\perp}$ are the values of the effective heat conductivity coefficient taking into account the pseudoturbulence in the porous body in the direction parallel and perpendicular to the gas flow.

Heat Transfer Coefficient. The effective internal heat transfer coefficient $\alpha_{t . g}$ with dimension $\mathrm{W} /\left(\mathrm{m}^{3} \cdot \mathrm{~K}\right)$ in a porous medium is calculated from the relation

$$
\frac{1}{\alpha_{\mathrm{t.g}}}=\frac{1}{\alpha_{\mathrm{g}} A_{\mathrm{t.g}}}+\frac{1}{\alpha_{\mathrm{t}} A_{\mathrm{t.g}}}
$$

where $A_{\mathrm{t} . \mathrm{g}}$ is the surface of a unit volume of the porous body (for a regular structure in the form of packed spheres of diameter $\left.d_{\mathrm{t}}, A_{\mathrm{t} . \mathrm{g}}=6(1-\varepsilon) / d_{\mathrm{t}}\right) ; \alpha_{\mathrm{g}}$ is the ordinary heat transfer coefficient between the porous medium particle and the gas, and $\alpha_{\mathrm{t}}$ reflects the internal thermal resistance of the solid particle of the porous body.

The calculation of $\alpha_{t}$ is based on the solution of the heat conduction equation for a solid particle with a boundary condition of the third kind, the regular thermal conditions being considered thereby (i.e., only the first eigenvalue is used). The value of $\alpha_{t}$ is calculated in terms of the ratio of the heat flow to the difference between the surface temperature of the particle and its average temperature. At $\mathrm{Bi}=\infty, \alpha_{\mathrm{t}}=\frac{2}{3} \pi^{2} \lambda_{\mathrm{t}}$, which corresponds to the result obtained in [18]. Importantly, the influence of the shape of the particle on the $\alpha_{t}$ value is weak.

Kinetic Equations. The volume reaction of rubber pyrolysis obeys the kinetic equation

$$
\begin{equation*}
\frac{\partial \rho_{\mathrm{r}}}{\partial \tau}=-\rho_{\mathrm{r}} K_{\mathrm{r}} \exp \left(-\frac{E_{\mathrm{r}}}{R T_{\mathrm{t}}}\right) \tag{14}
\end{equation*}
$$

where $K_{\mathrm{r}}$ and $E_{\mathrm{r}}$ are reaction constants.
The reaction of carbon formation is also volume. It does not participate in the above thermal balance. Its kinetic equation is

$$
\begin{equation*}
\frac{\partial \rho_{\mathrm{c}}}{\partial \tau}=-\varphi \frac{\partial \rho_{\mathrm{r}}}{\partial \tau} \tag{15}
\end{equation*}
$$

Here $\varphi$ is the so-called "coke" defined determined as the ratio of the rates of the reaction of solid carbon residue formation to the rate of decrease in the rubber mass. Upon complete decomposition of the rubber the rate of the carbon formation reaction tends to zero.


Fig. 1. Measured temperature dependences of the relative mass of undecomposed rubber: $1-3$ ) data of [19] [1) natural rubber NR, 2) butadiene rubber $\mathrm{BR}, 3$ ) styrene-butadiene rubber SBR$]$; 4) data of [21]; 5) our data. $T_{\mathrm{t}},{ }^{\circ} \mathrm{C}$.

The change in the mass of water condensed on the tire surface in the reactor volume is due to the processes of condensation and evaporation

$$
\begin{equation*}
\varepsilon \frac{\partial \bar{\rho}_{\mathrm{w}}}{\partial \tau}=-J_{\mathrm{t} .}, \tag{16}
\end{equation*}
$$

where the flow $J_{\text {t.e }}$ is defined by formula (3); $\bar{\rho}_{\mathrm{w}}$ is the water mass referred to the volume of pores.
According to [19], the kinetic parameters of pyrolysis of tires in the nitrogen medium differed significantly depending on whether the side wall or a piece of the tire tread were chosen for analysis and on the kind of rubber used. Analysis of the change with time in the rubber density $\rho_{r}$ was performed in $[19,20]$ according to the kinetic equation

$$
\begin{equation*}
\frac{\partial \rho_{\mathrm{r}}}{\partial \tau}=-\sum_{i=1}^{i=N_{\mathrm{r}}} \rho_{\mathrm{r} i} K_{\mathrm{r} i} \exp \left(-\frac{E_{\mathrm{r} i}}{R T_{\mathrm{t}}}\right), \tag{17}
\end{equation*}
$$

where $\rho_{\mathrm{r} i}$ stands for the densities of different components $N_{\mathrm{r}}$ of the rubber $\sum_{i=1}^{N_{\mathrm{r}}} \rho_{\mathrm{r} i}=\rho_{\mathrm{r}}$.
The generalization of the results of measurements of the kinetic parameters $K_{\mathrm{r} i}$ and $E_{\mathrm{r} i}$ in [19, 20] for four different types of tires shows their wide variation. In natural rubber ( NR ) and butadiene rubber $(\mathrm{BR})$ the reaction rates are very low, and styrene-butadiene rubber (SBR), on the contrary, has a very large rate constant of the decomposition reaction. In actual fact, tires consist of a mixture of different rubbers and, therefore, the rate constants of the reaction of the mixture $\mathrm{NR} / \mathrm{SBR} / \mathrm{BR}$ coincide in order of magnitude with the corresponding values for the four different types of tires. The characteristic decomposition rate of tires is of the order of $10^{-3} \mathrm{sec}^{-1}$.

The spread of experimental values of kinetic parameters can apparently be explained by nothing but experimental errors. And, as was noted in [19], the characteristic "kinetic" time in the decomposition of tires is about two orders of magnitude shorter than the characteristic time determined by the heat conduction process. For this reason the approach in which the flow from the solid phase to the gas phase is determined by differentiating the known empirical temperature dependence of the relative mass of undecomposed rubber

$$
\begin{equation*}
\frac{M_{\mathrm{r}}}{M_{\mathrm{r} 0}}=f\left(T_{\mathrm{t}}\right) \tag{18}
\end{equation*}
$$

seems to be more reliable. Consequently, we can restrict ourselves to the "equilibrium" temperature dependence (18) of the undecomposed rubber mass. Examples of measured dependences (18) for various specimens of tires are given in Fig. 1.


Fig. 2. Derivative $d f\left(T_{\mathrm{t}}\right) / d T_{\mathrm{t}}$ constructed by the difference method for curves 4 and 5 in Fig. 1. $T_{\mathrm{t}},{ }^{\mathrm{o}} \mathrm{C}$.
Fig. 3. Differential thermogravitometric dependence $\frac{d f\left(T_{\mathrm{t}}\right)}{d T_{\mathrm{t}}} \frac{d T_{\mathrm{t}}}{d \tau}$ (in mass percent of undecomposed rubber per minute) as a function of the decomposition temperature. Designations of $1-3$ are same as in Fig. 1. T, ${ }^{\circ} \mathrm{C}$.

We shall further use the data of [21] and our results. Curves 4 and 5 in Fig. 1 are approximated by dependences in the form of splines. Along with the function $f\left(T_{\mathrm{t}}\right)$ we shall further need the function $d f\left(T_{\mathrm{t}}\right) / d T_{\mathrm{t}}$. Figure 2 shows this derivative constructed by the difference method for curves 4 and 5 in Fig. 1.

For comparison, we give the graph (Fig. 3) from [19] which shows the quantity $\frac{d f\left(T_{\mathrm{t}}\right)}{d T_{\mathrm{t}}} \frac{d T_{\mathrm{t}}}{d \tau}$ for curves 1-3 in Fig. 1.

Tires consisting, as a rule, of different kinds of rubber are characterized by the presence of several peaks in the function $d f\left(T_{\mathrm{t}}\right) / d T_{\mathrm{t}}$ associated with the decomposition of several components, which is seen from the curves in Figs. 2 and 3.

Thermophysical Properties of Materials. The values of the thermophysical properties of the mixture of gaseous products of rubber decomposition and steam are calculated by the formulas

$$
\frac{W_{\mathrm{g}}}{\mu_{\mathrm{g}}}=\frac{V_{\mathrm{e}}}{V_{\mathrm{g}}} \frac{W_{\mathrm{e}}}{\mu_{\mathrm{e}}}+\frac{V_{\mathrm{p}}}{V_{\mathrm{g}}} \frac{W_{\mathrm{p}}}{\mu_{\mathrm{p}}}, \quad C_{\mathrm{g}}=Y_{\mathrm{p}} C_{\mathrm{p}}+Y_{\mathrm{e}} C_{\mathrm{e}}, \quad \lambda_{\mathrm{g}}=\frac{V_{\mathrm{e}}}{V_{\mathrm{g}}} \lambda_{\mathrm{e}}+\frac{V_{\mathrm{p}}}{V_{\mathrm{g}}} \lambda_{\mathrm{p}}
$$

where $\lambda_{\mathrm{p}}=\lambda_{\mathrm{p} 0}\left(1+a_{\lambda} T\right) ; a_{\lambda}=0.0027 ; \lambda_{\mathrm{p} 0}=0.0243$.
The partial volumes are calculated according to the formulas

$$
\frac{V_{\mathrm{e}}}{V_{\mathrm{g}}}=\frac{Y_{\mathrm{e}} / W_{\mathrm{e}}}{\left(Y_{\mathrm{e}} / W_{\mathrm{e}}+Y_{\mathrm{p}} / W_{\mathrm{p}}\right)}, \quad \frac{V_{\mathrm{p}}}{V_{\mathrm{g}}}=\frac{Y_{\mathrm{p}} / W_{\mathrm{p}}}{\left(Y_{\mathrm{e}} / W_{\mathrm{e}}+Y_{\mathrm{p}} / W_{\mathrm{p}}\right)}
$$

The molecular mass of rubber decomposition products is determined by calculations on the basis of the data on boiling temperatures of petroleum products [21]

$$
\begin{gather*}
W_{\mathrm{p}}=-12272.6+9486.4 \rho_{\mathrm{p}}+(8.3741-5.991 \rho) T_{\mathrm{g}} \\
+\left(0.55556-0.42824 \rho_{\mathrm{p}}-0.011433 \rho_{\mathrm{p}}^{3}\right)\left(1.3437-\frac{400.43}{T_{\mathrm{g}}}\right) \frac{10^{7}}{T_{\mathrm{g}}} \\
+\left(0.1715-0.1387 \rho_{\mathrm{p}}+0.003317 \rho_{\mathrm{p}}^{2}\right)\left(1.8828-\frac{101.1}{T_{\mathrm{g}}}\right) \frac{10^{12}}{T_{\mathrm{g}}^{3}} \tag{19}
\end{gather*}
$$



Fig. 4. Time variation of the density of the steam-gas mixture introduced into the reactor. $\rho_{\text {p.inl }}, \mathrm{kg} / \mathrm{m}^{3} ; \tau$, sec.
where $\rho_{\mathrm{p}}$ is the partial density of rubber decomposition products; $T_{\mathrm{g}}$ is the temperature of the steam-gas mixture.
The dynamic viscosity of the steam and rubber decomposition products depending on the temperature vary in accordance with the Sutherland formula

$$
\mu_{k}=\mu_{k 0} \sqrt{\frac{T_{\mathrm{g}}}{T_{\mathrm{g} 0}}} \frac{1+B_{k} / T_{\mathrm{g} 0}}{1+B_{k} / T_{\mathrm{g}}}, \quad k=\mathrm{p}, \mathrm{e}
$$

where $B_{k}$ is the Sutherland constant and the index 0 pertains to reference conditions.
The total masses of the rubber vapors and steam, as well as the total mass of the gas are calculated as the integrals

$$
M_{\mathrm{p}}=\int \rho_{\mathrm{p}} d V, \quad M_{\mathrm{e}}=\int\left(\rho_{\mathrm{g}}-\rho_{\mathrm{p}}\right) d V, \quad M_{\mathrm{g}}=M_{\mathrm{p}}+M_{\mathrm{e}}=\int \rho_{\mathrm{g}} d V
$$

For the steam, the values of the isobaric heat capacity $C_{\mathrm{e}}$, heat conductivity $\lambda_{\mathrm{e}}$, and viscosity $\mu_{\mathrm{e}}$, are calculated by interpolation tables. The analogous values for the gaseous products of rubber decomposition are determined by the data of [20].

The density of tires is calculated by summing the densities of the rubber, coke, water, and metal cord. The heat capacity of tires as an additive property obeys the relation

$$
C_{\mathrm{t}}=\frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{t}}} C_{\mathrm{r}}+\frac{\rho_{\mathrm{m}}}{\rho_{\mathrm{t}}} C_{\mathrm{m}}+\frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{t}}} C_{\mathrm{w}}+\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{t}}} C_{\mathrm{c}}
$$

Reactor Parameters. The porosity is determined by the packing density of pieces of tires. For the calculated variants, it was assumed equal to $\varepsilon=0.4$. The base area of the reactor $S=2.4 \mathrm{~m}^{2}$, the height is 1.5 m , and the processing time is of the order of $\tau=6000 \mathrm{sec}$. The wall of the thermolysis chamber shared with the furnace had a temperature of $600^{\circ} \mathrm{C}$. At the entrance into the reactor the steam-gas mixture also had a temperature of $600^{\circ} \mathrm{C}$. The steam consumption was chosen from the relation 1 t of steam per 1 t of rubber. For these loading parameters, the linear velocity $u$ was $0.1 \mathrm{~m} / \mathrm{sec}$. The preheating chamber brings the temperature of tires up to the initial temperature $T_{\text {in }}=60^{\circ} \mathrm{C}$, which creates the initial conditions in the chamber. The pressure in the course of the thermolysis process is held at the level of 1.1 atm by means of regulation consisting of the fact that part of the consumed gaseous reaction product at the outlet from the reactor was extracted in the condenser. After this the remaining reaction product was conveyed again to the reactor inlet and fresh steam was added to this flow by means of a superheater.

In the calculations, such a working cycle was simulated by means of the approximate cyclic condition at the reactor inlet $Y_{\text {p.inl }}=Y_{\text {p.out }}$, since the chemical composition of the heating gas varied with time. At the start of the process it was pure steam, and at subsequent instants of time the mass fraction of the steam decreased due to an increase in the mass fraction of the rubber decomposition products.


Fig. 5. Undecomposed rubber density in the reactor at various instants of time: a) $\tau=2000 \mathrm{sec}$; b) 3000 ; c) $4000 . \rho_{\mathrm{r}}, \mathrm{kg} / \mathrm{m}^{3}$.


Fig. 6. Condensed water mass distribution in the reactor: a) $\tau=50 \mathrm{sec}$; b) 100. $M_{\mathrm{W}}, \mathrm{kg}$.

Figure 4 shows the change with time in the average mixture density over the area of the reactor base through which the gas is let in.

The process of decomposition of tires lasts for a little more than 4000 sec . In this period the density of the mixture at the inlet increases due to the change in its mass composition and the higher molecular weight of the rubber decomposition products compared to the steam. In the rest of the period the density decreases to the value corresponding to pure steam at given temperature and pressure. The characteristic dip of the curve with a minimum at $\tau=500$ sec in this time interval is due to the intensive evaporation of the water accumulated on the surface of tires in the initial period of steam condensation on cold tires. At the outlet from the reactor the mass content of steam increases and the steam-gas mixture density decreases.

Results and Discussion. Let us first give a few two-dimensional distributions. Figure 5 shows the mass distribution of undecomposed rubber in the reactor. (The initial rubber density is $959 \mathrm{~kg} / \mathrm{m}^{3}$.) It is seen that at intermediate instants of time (at $\tau=2000 \mathrm{sec}$ ) this distribution is nonuniform. The most unfavorable for the reaction zone is situated in the upper part of the reactor on its axis where the temperature of tires is minimal, since the temperature of waste steam decreases with height and the wall (in the figures on the left) is heated to a higher temperature. In the course of time the temperature field along the reactor radius becomes homogeneous, as a result of which the rubber concentration field becomes one-dimensional and largely depends on the reactor position in height.


Fig. 7. Time variation of the condensed water mass in the reactor. $M_{\mathrm{W}}, \mathrm{kg} ; \tau$, sec.
Fig. 8. Temperatures of the tires $T_{\mathrm{t}}$, the steam-gas mixture $T_{\mathrm{g}}$, and the tire-gas interface $T_{\mathrm{t} . \mathrm{g}}$ as a function of time. $T, \mathrm{~K} ; \tau$, sec.



Fig. 9. Convective $\alpha_{g}$ and conductive $\alpha_{t}$ heat transfer coefficients as a function of time. $\alpha, \mathrm{W} /\left(\mathrm{m}^{2} \cdot \mathrm{~K}\right) ; \tau$, sec.
Fig. 10. Intensity of convective heat exchange between the tires and the steamgas mixture as a function of time. $\alpha_{\mathrm{t} . \mathrm{g}}\left(T_{\mathrm{t}}-T_{\mathrm{g}}\right), \mathrm{W} / \mathrm{m}^{3} ; \tau$, sec.

The influence of the moisture condensed from the steam manifests itself in a short time measured to be about 150 sec . Figure 6 shows the distribution of the condensed moisture mass at two instants of time. It is seen that in the course of time the quantity of moisture decreases. Its maximum condenses in the lower part of the reactor, on its axis.

The total quantity of condensed moisture has a maximum when the process proceeds for about 100 sec (Fig. 7). While it is possible to distinguish the influence of this quantity of moisture on the temperature characteristics of the process, the calculations performed permit, in general, stating that the action of this factor is transient. Apparently, the considerable quantity of moisture on the surface of tires visually observed in the experiment should be attributed to the liquid products of rubber decomposition rather than to the condensed moisture.

Figure 8 shows the evolution of the reactor-volume-averaged temperatures of tires, the gas, and the gas-tire interface surface. The decomposition process proceeds for about 4500 sec , after which all the three temperatures become homogeneous in the absence of chemical source terms from the corresponding balance equation of the tire temperature. Upon completion of the decomposition process the gas temperature increases, and the average temperature of tires and the tire surface temperature tend to the gas temperature.

The average temperature of the tire surface in Fig. 8 turns out to be close to the gas temperature, differing from it by no more than $50^{\circ} \mathrm{C}$. The reason is that the thermal resistance of the tire itself considerably exceeds the thermal resistance of the convective heat exchange in the porous body.

The values of the reactor-volume-average convective and conductive heat transfer coefficients as functions of time are given in Fig. 9. It is seen that at different instants of time the convective heat transfer coefficient is from two


Fig. 11. Masses of undecomposed rubber $M_{\mathrm{r}}$ and formed coke $M_{\mathrm{c}}$ as a function of time. $M, \mathrm{~kg} ; \tau$, sec.
Fig. 12. Integrated intensity of rubber decomposition in the reactor as a function of time. $\tau$, sec.
to seven times higher than the conductive one. The conductive coefficient is time-invariable, since the form of the tires remains unaltered and the coke formed has a poor heat conduction as does the rubber. The convective heat transfer coefficient is connected with a large number of temperature-dependent factors - properties of the medium. Upon completion of the reaction this coefficient increases more than twice.

The change with time in the average integrated intensity of steam-tire heat transfer is illustrated in Fig. 10. In general, it decreases steadily, and upon completion of the reaction tends to zero since the temperature difference "porous body skeleton-gas" tends to zero. At this moment the coked residue and the metal cord act as a porous body skeleton.

Figure 11 shows the main technological parameter - undecomposed rubber mass. This figure also shows the growth with time of the coke residue mass. Note that the calculated time of the technological process is in good agreement with the experiment.

The decomposition rate of the rubber of tires is shown in Fig. 12. The value of $\int_{V} \cdot J_{\mathrm{t} . \mathrm{p}} d V$ correlates well with the differential thermogravitometric dependence in Fig. 3. The peaks of the decomposition rate of tires appear at average temperatures of tires about 250 and $500^{\circ} \mathrm{C}$.

Conclusions. The numerical study made has enabled us to describe the change with time in the rubber decomposition by steam thermolysis at different stages of the reaction up to its completion. Unlike the earlier works devoted to this method [11, 12], nonstationary two-dimensional simulation of a cylindrical reactor has been performed. The approach used makes it possible to revise the existing notions on the process and reveal factors promoting or retarding the reaction. The influence of the process of condensation and subsequent evaporation of water manifests itself in a rather short time of about 2 min and, therefore, does not lead to a change in the thermal and time characteristics of the process. Good qualitative agreement with the recorded parameters of the real technological process, in particular, with the process duration and the temperature field in the reactor has been obtained. The decisive influence on the process duration of the conductive heat resistance of tires depending also on the tire comminution parameters before processing has been noted.

## NOTATION

$A_{\mathrm{t} . \mathrm{g}}$, specific surface; Bi , Biot criterion; $C$, specific heat capacity; $d_{\mathrm{t}}$, characteristic size of pieces of tires; $D$, diffusion coefficient; $J$, intensity of interphase transitions, $\mathrm{kg} /\left(\mathrm{m}^{3} \cdot \mathrm{sec}\right) ; K$, permeability coefficient; $M$, mass; $P$, pressure; Pe , Peclet criterion; $Q_{\mathrm{e}}$, heat of phase transition; $Q_{\mathrm{p}}$, thermolysis heat; $\mathrm{Re}=\rho_{\mathrm{g}} w d_{\mathrm{t}} /\left(\mu_{\mathrm{g}} \varepsilon\right)$, Reynolds criterion; Sc $=\mu_{\mathrm{g}} /\left(\rho_{\mathrm{g}} D\right)$, Schmidt criterion; $T$, temperature; $V$, volume; w, speed of filtration; $W$, molecular weight; $Y$, mass concentration; $\alpha$, heat transfer coefficient; $\varepsilon$, porosity; $\lambda$, heat conductivity coefficient; $\mu$, viscosity; $\rho$, density; $\tau$, time.

Subscripts: $g$, gas; $t$, solid body; t.g, interface of phases $g$ and $t$; $e$, steam; $r$, rubber; $m$, metal; $c$, coke; p, gaseous products of rubber decomposition; s, saturation; w, water; in, initial; eff, effective; inl, inlet; out, outlet.

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