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HEAT TREATMENT OF ORGANIC POLYMERS IN A FLOW OF A GASEOUS HEAT CARRIER

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Processes of heat and mass transfer are studied during heat treatment of organic polymers in a superheated-steam flow. Promising environmentally safe engineering processes of treatment of plant biomass, plastics, and rubber wastes that contain petroleum products of sludges and soils are described.

A large number of studies are devoted to problems of heat and mass transfer in treatment of organic materials in a vapor–gas flow. Primarily, one should mention works by A. V. Luikov and his students and followers that have already become classical and in which an approach to the description of heat and mass transfer processes occurring during drying of porous and disperse materials by superheated steam or vapor–gas mixtures was developed [1]. However, attention should be paid to the fact that this approach is applicable to processes occurring in a diffusion region and necessitates experimental determination of a large number of thermodynamic parameters, which is a complex problem.

To describe high-intensity heat and mass transfer processes occurring under vapor-thermal action on organic materials with disperse and porous structures an approach is used whose principles were developed in the theory of nonisothermal multicomponent filtration [2, 3]. However, formulation and solution of problems within the framework of this approach involve serious mathematical difficulties due to the complex character of the systems of equations and the formulation of the boundary conditions.

A large number of scientific papers are devoted to the study of heat and mass transfer processes in organic materials by balance methods based on equations of thermal and material balance. They are widely used in calculations of pyrolysis and gasification of organic materials.

It follows from an analysis of the literature devoted to heat and mass transfer processes during heat treatment of organic materials in a flow of a gaseous heat carrier that no unique theoretical approach has been developed up to now, and there are no adequate physical or mathematical models, especially for processes occurring in heat treatment of organic materials in a superheated-steam flow.

We performed a complex of works directed to a study of heat and mass transfer processes and physicochemical conversions under the action of superheated steam on different organic polymers.

Plant biomass, whose annual worldwide growth reaches 170–200 billion tons (in terms of dry mass), is the most abundant natural organic material.

Recently, technologies for plant biomass treatment have especially intensely, and great success has been achieved in this direction. Due to the possibility of continuous recovery special attention is paid to the trend involving development of new highly efficient technologies for energetic utilization of plant biomass [4].

Here a considerable economic and environmental effect is attained since plant biomass, as an energy source, does not affect the balance of carbon dioxide in the atmosphere, which distinguishes it from other types of fuel. Wide use of plant biomass in power engineering is impeded by the absence of highly efficient and environmentally safe technologies. Development of these technologies is tied to the solution of a number of problems involving thermal decomposition of biomass and heat transfer in complex systems with disperse and porous structures.

Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute of the Academy of Sciences of Belarus," Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 69, No. 6, pp. 1021-1025, November-December, 1966. Original article submitted September 9, 1996.

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TABLE 1. Physicochemical Parameters of Heat Treatment of Plant Biomass in a Superheated Steam Flow

Parameters	Heating temperature, °C				
	205	210	215	220	225
Endothermic effect, MJ/kg	0.242	0.450	0.656	0.863	1.069
Ratio $\Delta Q_{\text{end}}/Q_{\text{heat}}$	0.68	1.25	1.77	2.27	2.74
Specific heat of combustion of treated biomass, $Q_{\text{low,fin}}^{\text{work}}$, MJ/kg	19.829	20.050	20.280	20.491	20.730
Specific heat of combustion of volatiles, $Q_{\text{comb}}^{\text{vol}}$, MJ/kg	11.90	12.20	12.49	12.79	13.10

A promising direction of energetic utilization of biomass is its heat treatment in a superheated-steam flow. A complex of studies carried out shows that in this way thermal processes (drying, thermal decomposition, pyrolysis) can be enhanced substantially, harmful discharges into the environment can be reduced, and high-quality solid fuel and adsorption materials can be obtained [5, 6].

Heat treatment of plant biomass was studied by a technique that makes it possible to simultaneously and continuously record pressure, temperature, and saturation under the action of superheated steam or a vapor–gas mixture on disperse organic material [3]. An analysis of the results obtained allows one to distinguish specific features of this process.

Initially steam is intensely condensed on the surface of the plant biomass sample, and the precipitated condensate is absorbed by it. Estimates show that at the initial stage the quantity of condensate corresponds to the quantity of steam that must be condensed in order that the heat of condensation liberated here be sufficient to heat up the biomass to the saturation temperature.

When the biomass is heated to the saturation temperature steam condensation ceases and the process of moisture evaporation begins due to the superheating. At the instant when the biomass temperature reaches some value (it depends on the type of biomass), the process of thermal decomposition begins, which is accompanied at the first stage by the effect of heat absorption. To determine quantitatively the magnitude of this effect a technique is suggested that consists in determination of the heat of combustion of the formed products and calculation of the endothermic effect by the relation

$$\Delta Q_{\text{end}} = M_{\text{fin}}^{0} Q_{\text{low,fin}}^{\text{work}} + Q_{\text{comb}}^{\text{vol}} - Q_{\text{low}}^{\text{work}} . \tag{1}$$

The studies show that in heat treatment of plant biomass (wood wastes) with an initial elemental composition of carbon 50.58, hydrogen 6.42, and oxygen 43 wt.% in a superheated-steam flow the physicochemical parameters depend on the temperature of the treatment (see Table 1).

As follows from an analysis of the table the value of the endothermic effect depends considerably on the temperature of biomass heating; as the temperature is changed from 200 to 225°C the quantity of absorbed heat increases more than fourfold. The endothermic heat at $t = 225°C$ is 2.74 times higher than the heat spent for heating the biomass to this temperature. Growth of the specific heat of combustion of the steam-treated biomass is observed, thus indicating biomass enrichment by combustible elements.

The elemental composition of wood wastes changes upon heating in a steam medium to $t = 220°C$ and becomes the following: carbon 56.9, hydrogen 5.13, and oxygen 37.97 wt.%. Here the mass of volatile products per kg of absolutely dry wood varies depending on the treatment temperature and is 0.0825 kg at $t_{\text{tr}} = 205°C$ and 0.922 kg at $t_{\text{tr}} = 220°C$.

Thus, thermal decomposition accompanied by the effects of heat absorption and mass transfer (escape of volatiles) occurs under the action of superheated steam.

These effects can be substantial in value and they affect considerably the process of heat and mass transfer in the system of superheated steam and plant biomass.

It is seen from an analysis of experimental data that after evaporation of precipitated condensate the process of heat transfer from the superheated-steam flow to the surface of the crushed biomass is rather well described by the relation

$$\overline{\mathrm{Nu}} = 0.58\,\mathrm{Re}^{0.65}\,, \tag{2}$$

Here the rate of superheated-steam filtration is found by the relation

$$\overline{V}_{\mathrm{st}} = \frac{K}{\mu_{\mathrm{st}}}\,\frac{P_{\mathrm{inl}} - P_{\mathrm{ex}}}{H_{\mathrm{layer}}}\,. \tag{3}$$

Recently, problems of utilization of plastic wastes have acquired high priority. The main trends in treatment of these wastes are pyrolysis, depolymerization with formation of the initial products, and secondary treatment. However, each of these trends has certain drawbacks. For example, secondary treatment of contaminated industrial and household plastic wastes requires removing impurities from them, sorting, and pressing and is very laborious.

Heat treatment of polymer wastes in a superheated-steam flow without their preliminary sorting or cleaning with production of products for chemical-engineering and power-engineering purposes, seems to be promising. To substantiate this possibility, a complex of studies of the laws governing physicochemical conversions and heat and mass transfer processes was conducted. It is found that the heat treatment conditions (rate of heating, temperature, steam pressure) and the initial state of the polymer (dispersity, humidity, degree and type of contamination, composition of an initial mixture) affect considerably the properties of the products produced and the energetic and environmental efficiency of the process.

The presence of disperse inert material in the system of superheated steam and polymer organic wastes leads to the effect of separation of the waste melt by density and enhancement of heat transfer processes, thus resulting in acceleration of the physicochemical conversions. The process is represented as follows. Being in contact with superheated steam and disperse material, the polymers are heated and melted. The melt impregnates the disperse material and envelops its particles; as a result the specific surface of interaction between the steam and the melt is developed and heat and mass transfer is enhanced. Simultaneously thermal decomposition of the wastes takes place [7].

Engineering use of thermal decomposition of polymer wastes in a superheated-steam flow is possible by two main ways of utilization that determine the economic efficiency of the process. In the first case the main purpose is to obtain high-quality gaseous, liquid, and solid fuels and oils, and in the second case chemical raw materials, mainly olefins and aromatic hydrocarbons.

In a total amount of production and consumption wastes to be treated a considerable portion is composed of different sludges and soils that are disperse inorganic materials mixed with different organic substances, including petroleum products. At present, the main methods of utilization of these wastes are their storage or combustion in special furnaces. Among promising methods of treatment of such wastes is heat treatment by steam, which results in separation into inorganic and organic components [8].

Experimental studies of the process of heat treatment of wastes were conducted within a wide range of variation of temperature, duration, and steam flow rate for different quantities of organic materials in the initial material.

An analysis of the results obtained shows that heat treatment of disperse materials that contain organic substances in a superheated-steam flow allows their complete separation.

Utilization of rubber wastes and, in particular, automobile tires is an important environmental and economic problem. In spite of the variety of techniques for treating such wastes that are known at present, this problem has not been solved as yet at a sufficiently high environmental and economic level. A promising trend is the development of technological processes based on thermal techniques of treatment of rubber-containing materials. A highly efficient technology can be created by means of heat treatment of rubber wastes in a superheated-steam flow as a result of which they are decomposed into solid, liquid, and gaseous products at temperatures of 400–500°C [9]. Experiments with samples of automobile tires with a metallic cord show that the formed products contain liquid hydrocarbons (35–50 wt.%), gaseous hydrocarbons (8–6 wt.%), carbon-containing residue (50–38 wt.%), and metal (6–10 wt.%). The heat of combustion of the liquid hydrocarbons attains 41 MJ/kg, that of the carbon-containing residue 36 MJ/kg, and that of the gaseous products 24–30 MJ/kg.

By mixing liquid and solid products of decomposition of 1 ton of rubber wastes with condensate (water) one can obtain using this method up to 1900 kg of fuel with a heat of combustion $Q_{\text{low}}^{\text{work}} = 15-16$ MJ/kg. Studies of properties of carbon-containing residue formed as a result of heat treatment of rubber-containing and other organic polymers show that, with a certain organization of the process, one can obtain activated charcoal.

Thus, the idea of heat treatment of organic polymers in a superheated-steam flow offers the possibility of using them as energetic fuel or raw material for chemical production and also of developing efficient environmentally safe technological processes [10].

NOTATION

ΔQ_{end}, endothermic effect; $M_{\text{fin}}^{0} = M_{\text{fin}}/M_{\text{in}}$, relative mass; $Q_{\text{low,fin}}^{\text{work}}$, specific heat of combustion of the treated biomass; $Q_{\text{comb}}^{\text{vol}}$, specific heat of combustion of the volatile products; $Q_{\text{low}}^{\text{work}}$, specific heat of combustion of the initial biomass; α, coefficient of heat transfer; d_{p}, diameter of the particles; λ_{st}, thermal conductivity of the steam; ν_{st}, kinematic viscosity of the steam; μ_{st}, dynamic viscosity of the steam; V_{st}, velocity of the steam; K, permeability; P_{inl}, pressure at the inlet; P_{ex}, pressure at the exit; H_{layer}, layer height; Nu, Nusselt number; Re, Reynolds number; $\text{Nu} = \alpha d_{\text{p}}/\lambda_{\text{st}}$; $\text{Re} = V_{\text{st}} d_{\text{p}}/\nu_{\text{st}}$. Subscripts and superscripts: fin, final products, in, initial products; low, lower; work, working; vol, volatile; comb, combustion; p, particle; st, steam; heat, heating.

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