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OBTAINING OF FUELS BASED ON PRODUCTS OF ORGANIC-WASTE STEAM THERMOLYSIS

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A technological line for thermolysis of technical rubber waste and biomass in the medium of superheated steam is considered. The characteristics of fuels based on liquid- and solid-waste thermolysis products are given, and the energy efficiency of obtaining composite fuels has been estimated.

Introduction. Analysis of the waste-formation dynamics leads to the conclusion that further development of production cannot proceed without taking into account ecological aspects connected with the accumulation of waste. At present, up to 2/3 of waste can be recycled, and in the future production should be based on recoverable refuse.

In the Republic of Belarus, over 24 million tons of production and consumption waste are formed annually, including 2.4 million tons of wood waste, 60 thousand tons of used tires, and up to 50 thousand tons of recoverable polyethylene refuse. It should be noted that, for making products and generating energy, only 16% of the whole mass of waste are used and the remaining part is accumulated in the territory of Belarus and now amounts to about 640 million tons, and over 3000 ha of land are occupied by dumps [1].

The biomass of vegetable and animal origin, the forestry and wood-working industry waste, and solid and liquid organic waste are considered worldwide as the most important (under the present-day conditions) nontraditional recoverable source of energy and raw materials.

The biomass is being used more and more for energy purposes in industrial countries. In the European Union countries, about 3% (65 million tons of equivalent fuel) of the total energy requirement are satisfied at the cost of the biomass, and in individual countries this index reaches 23% (Finland), 18% (Sweden), and 12% (Austria).

The present-day thermal technologies of obtaining fuel, energy, and raw materials from waste are based on the processes of combustion, gasification, pyrolysis, liquefaction (obtaining of synthetic fuels), thermobriquetting, etc.

Analyzing waste-management technologies, it may be concluded that the most promising direction in developing high-efficiency and ecologically clean methods of processing them is the direction connected with the thermal methods of waste reclamation. In the last few years, as a result of the intensification of investigations on the problems of waste management, a number of technological processes and apparatuses for obtaining raw materials and energy resources from it have been proposed. At the same time, most of the technologies and equipment used are low-efficiency, material-intensive, or very expensive, and the directions of using processing products do not provide the necessary economic efficiency mainly because of the low quality of the products obtained.

In the present paper, with the example of using the technological line for organic-waste thermolysis in the medium of superheated steam, the process of obtaining composite fuel has been considered and the good prospects for vapor thermolysis as a technique of thermal processing of a wide spectrum of waste have been substantiated.

Technological Line for Steam Thermolysis of Waste. The technological line for organic-waste thermolysis in the medium of superheated steam is schematically represented in Fig. 1.

Organic waste (used tires, biomass), without preliminary comminution, from the loading bin 1 is placed on technological trolleys 2 and supplied to the preheating chamber 3. The waste heated to a temperature of $60-100^{\circ}$ C goes further to the thermolysis chamber 4. Loading of waste and removal of products from the thermolysis chamber are carried out portionwise through gates 5. From the steam generator 6 the steam superheated in the steam generator

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Fig. 1. Process chart for organic-waste thermolysis in the medium of superheated steam: a) steam-gas mixture; b) nonconcentrated gas; c) liquid hydrocarbon product; d) water and steam; e) metal cord and technical carbon.

7 is supplied additionally to the thermolysis chamber. The steam collectors ensure a uniform distribution of steam in the reaction zone. The decomposition process proceeds at a temperature of $300-700^{\circ}$ C and a pressure of 1-1.2 atm. The steam-gas mixture containing gaseous products of waste decomposition is carried from the chamber to the two-stage condenser 8. Condensed products are collected in the tank collecting liquid fractions 9.

The liquid hydrocarbon fraction is separated from the condensed steam and conveyed to the vessel 10. After additional purification in the reservoir 11, the water is conveyed to the steam generator 6 and returns into the process. The noncondensed gaseous fraction is conveyed to the furnace of the facility 12 for burning. The duration of the decomposition process is from 1 to 3 h, depending on the kind of waste and the size of the tires. On completion of the process, the trolleys are moved into the cooling chamber 13, cooled down to a temperature of 70–80°C, and then go to remove the carbon residual. The obtained carbon is separated from the metal cord in the separator 14, and both products are stored in the accumulators 15 and 16.

Upon unloading, the technological trolleys with the use of the hoisting device 17 return to the loading stage. Steam thermolysis yields the following products: gaseous hydrocarbons (8–40 mass %), liquid hydrocarbons (20–45 mass %), carbon residual (25–40 mass %), and metal cord (up to 20 mass % in the case of tire processing), depending on the kind of waste being processed.

The investigation of the process of steam thermolysis has shown that an increase in the temperature in the thermal-decomposition zone leads to a sharp increase in the yield of liquid and gaseous products and a marked decrease in the quantity of the carbon residual formed [2].

Energy and Material Balance of the Thermolysis Process. The total quantity of heat needed for thermal decomposition of waste in the thermolysis chamber is determined as follows:

$$Q_{\text{total}} = Q_{\text{h}} + Q_{\text{d}} + Q_{\text{loss}} \tag{1}$$

or

$$Q_{\text{total}} = 1.2 \cdot \left[C_{p\text{waste}} M_{\text{waste}} \left(T_{\text{waste}}^{(2)} - T_{\text{waste}}^{(1)} \right) + r_{\text{waste}} M_{\text{waste}} \right],$$
(2)

since the heat loss Q_{loss} is about 20%.

For $C_{pwaste} = 1.4 \text{ kJ/(kg.°C)}$, $M_{waste} = 400 \text{ kg}$, $T_{waste}^{(2)} = 500^{\circ}\text{C}$, $T_{waste}^{(1)} = 100^{\circ}\text{C}$, and $r_{waste} = 600 \text{ kJ/kg}$, from (2) we determine $Q_{\text{total}} = 556,800 \text{ kJ}$.

To produce 200 kg/h of steam, liquid fuel is burned in the furnace at a flow rate of 18 kg/h and the fuelcombustion products are conveyed at a rate of 220 kg/h (combustion of 1 kg of fuel produces 12.2 kg of combustion products) into the chimney. To superheat 200 kg/h of steam from 140 to 665° C, 13.5 kg/h of fuel are burned up, and the products of the fuel combustion in the furnace (temperature 800° C) are conveyed to the chimney at a rate of 165 kg/h through the thermolysis chamber jacket and the preheating chambers. The temperature of gases released into the environment is in the 200–250°C range. The quantity of heat transferred from combustion products to the thermolysis chamber is equal to

$$Q_{\rm com,p}^{(t)} = M_{\rm comp} C_{\rm comp} \left(T_{\rm comp}^{(2)} - T_{\rm comp}^{(1)} \right).$$
(3)

For $M_{\text{com},p} = 165 \text{ kg/h}$, $C_{\text{com},p} = 1.34 \text{ kJ/(kg·°C)}$, $T_{\text{com},p}^{(2)} = 800^{\circ}\text{C}$, $T_{\text{com},p}^{(1)} = 500^{\circ}\text{C}$, we obtain $Q_{\text{com},p} = 330 \text{ kJ/h}$.

In the preheating chamber, the heat from combustion products is transferred to the rubber waste. Its quantity is

$$Q_{\text{com},p}^{(\text{pr})} = M_{\text{com},p} C_{\text{com},p} \left(T_{\text{com},p}^{(1)} - T_{\text{com},p}^{(3)} \right).$$
(4)

For $T_{\text{com.p}}^{(3)} = 250^{\circ}\text{C}$ and $T_{\text{com.p}}^{(1)} = 500^{\circ}\text{C}$ we obtain $Q_{\text{com.p}}^{(s)} = 55,275$ kJ/h.

Since the furnace shares a wall with the thermolysis chamber, the heat from the wall is transferred convectively and radiationally (the wall is heated to 800° C) to worn tires, and the quantity of this heat constitutes 25% of the heat released in the furnace upon combustion of 13.5 kg/h of liquid fuel, i.e., the given quantity of heat is equal to 0.25·13.5 kg/h·44,440 kJ/kg = 150,000 kJ/h, where 44,440 kJ/kg is the specific heat of liquid fuel combustion.

Heat is conveyed to the thermolysis chamber (150,000 kJ/h) through the furnace wall, and 66,330 kJ/h — through the chamber jacket from the products of fuel combustion in the furnace. In 120 min, the thermolysis chamber will receive (150,000 kJ/h + 66,330 kJ/h)·2 h = 432,660 kJ of heat. To provide thermolysis with superheated steam (556,800–432,660) kJ = 124,410 kJ of heat should be transferred. Consequently, the required quantity of superheated steam with parameters $T_s^{(1)} = 665^{\circ}$ C, $T_s^{(2)} = 500^{\circ}$ C, and $C_{ps} = 2 \text{ kJ/(kg. °C)}$ will be $G_s = 200 \text{ kg/h}$.

In the thermolysis chamber, as a result of the heat exchange with the steam-gas medium, heating of worn tires up to a temperature of 300° C proceeds for 60 min and the process of thermal decomposition of rubber begins and proceeds for 60 min.

In our case, gaseous (160 kg) and solid (240 kg) decomposition products of worn tires are formed. The gaseous products are conveyed to the condenser. In the condenser, they and the steam are cooled, as a result of which the steam and part of the gaseous decomposition products are condensed to form water and a liquid fraction.

Let 90% of the gaseous products, i.e., $0.9 \cdot 160 \text{ kg/h} = 144 \text{ kg/h}$ (the condensation process proceeds for 2 h), be condensed. The condensation heat of these products is 300 kg/kg, and their heat capacity in the gaseous state is 3 kg/(kg·°C).

In this case, in the condenser, as a result of the cooling and condensation of a part of the steam-gas products, the following quantity of heat is released:

$$Q_{s,g} = C_{ps,g} M_{s,g} \left(T_{s,g}^{(1)} - T_{s,g}^{(2)} \right) + q_{s,g} M_{s,g} .$$
⁽⁵⁾

For $C_{ps,g} = 3 \text{ kJ/(kg.^{o}C)}, M_{s,g} = 72 \text{ kg/h}, T_{s,g}^{(1)} = 500^{\circ}C, T_{s,g}^{(2)} = 100^{\circ}C, q_{s,g} = 300 \text{ kJ/kg}$, we obtain $Q_{s,g} = 108,000 \text{ kJ/h}$.

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In the condenser, 200 kg/h of steam are cooled and condensed simultaneously. And the quantity of released heat thereby is equal to

$$Q_{\rm s} = C_{ps} M_{\rm s} \left(T_{\rm s}^{(1)} - T_{\rm s.g}^{(2)} \right) + q_{\rm s} M_{\rm s} \,. \tag{6}$$

For $C_{ps} = 2 \text{ kJ/(kg} \cdot ^{\circ}\text{C})$, $M_s = 200 \text{ kg/h}$, $T_s^{(1)} = 500^{\circ}\text{C}$, $T_{s,g}^{(2)} = 100^{\circ}\text{C}$, and $q_s = 2500 \text{ kJ/kg}$, we obtain $Q_s = 660,000 \text{ kJ/h}$.

Thus, in the condenser it is necessary to remove 108,000 kJ/h + 660,000 kJ/h = 768,000 kJ/h of heat. To this end, the following quantity of cooling water is needed:

$$M_{\rm c.w.con} = 768\ 000/C_{pc.w} \left(T_{\rm c.w.con}^{(2)} - T_{\rm c.w.con}^{(1)} \right).$$
(7)

For $C_{pc.w} = 4.18 \text{ kJ/(kg.}^{\circ}\text{C})$, $T_{c.w.con}^{(1)} = 30^{\circ}\text{C}$, $T_{c.w.con}^{(2)} = 80^{\circ}\text{C}$, we obtain $M_{c.w.con} = 3647 \text{ kg/h}$.

The 272 kg/h of water-oil mixture formed are conveyed from the condenser to the separator. At the separation stage, the mixture is split into 72 kg/h of a liquid hydrocarbon product and 200 kg/h of water, which, upon purification, is returned to the process for obtaining working steam.

The noncondensed gaseous products of thermal decomposition at the rate of 16 kg/h (the combustion heat is 22,200 kJ/kg) are conveyed to the steam-generator furnace and burned up. In so doing, the consumption of the fuel fed into the steam-generator furnace is reduced to 10 kg/h.

Upon completion of the process of thermal decomposition of worn tires, the solid decomposition products are transferred from the thermolysis chamber into the cooling chamber and cooled by water atomization. The steam produced is conveyed to the thermolysis chamber.

Along with the steam, the solid residual cooling heat returns into the thermolysis chamber, which leads to a reduction of the energy expended in processing the rubber waste.

To cool solid products from 500 to 100° C, the following quantity of water is needed:

$$M_{\rm c.w.sol} = C_{psol} M_{\rm sol} \left(T_{\rm sol}^{(2)} - T_{\rm sol}^{(1)} \right) / \left[C_{pc.w.sol} \left(T_{\rm c.w.sol}^{(2)} - T_{\rm c.w.sol}^{(1)} \right) + q_{\rm s} \right].$$
(8)

For $C_{psol} = 0.8$ kJ/kg and $M_{sol} = 120$ kg/h, we obtain $M_{c.w.sol} = 13.7$ kg/h.

Upon cooling down to 100°C, the solid products are transferred from the cooling chamber into the separator and then the metal is separated from the carboniferous residual.

Composite Liquid Fuel. Liquid-waste thermolysis products are analogous in their composition and properties to fuel oil with a combustion heat of about 42,000 kJ/kg. Solid products (carbonizate (semi-coke) made of particles less than 0.2 or 0.5 mm in size have a combustion heat of 33,000–37,000 kJ/kg, an ash content of 6.1%, and the following yield of volatile compounds: 45 and 35% (upon heating up to 1000 and 500°C, respectively).

Mixing of liquid and solid products leads to the formation of a slightly stable suspension (that segregates) at a component ratio of 70% (liq) + 30% (sol) and a stable suspension (that does not segregate) at a component ratio of 50% (liq) + 50% (sol).

As to the combustion heat, sulfur content, moisture, viscosity, and flash temperature, the composite liquid fuel (CLF) is close to boiler oils M40 and M100.

The CLF viscosity increases with increasing concentration of the solid phase and decreases as the temperature is increased to 80°C. The addition of sawdust or peat leads to a considerable increase in the viscosity, which makes it possible to control it and improve the ecological indices in the process of fuel combustion. In the process of fuel combustion, sulfur dioxide is bound by the ash components of the additive, which leads to a reduction of the content of harmful substances released into the atmosphere.

According to the quality certificate, the CLF based on products of thermal processing of worn tires consists of 50% liquid products, 45% solid products, and up to 5% sawdust or peat. With this ratio the effective viscosity at 60–80°C is equal to 0.4–0.7 Pa·sec; the flash temperature is 125° C; the elemental composition per combustible mass is C ~ 88, H ~ 8.8; S ~ 0.85; the moisture is 0.6%; the ash content is 3.7%; the lower combustion heat is 37,000 kJ/kg.

	Composite liquid fuel					Initial product	
Fuel parameters	l < 0.2 mm		l < 0.5 mm				
	Component ratio (liquid/solid/sawdust)					solid	liquid
	70/30/0	50/50/0	70/30/0	50/50/0	70/25/5		
Content of elements							
С	88	88	87	89	86	90	87
Н	10.37	8.90	10.0	9.0	10	5.6	12.6
S	0.90	0.91	0.80	0.91	0.8	1.00	0.4
Combustion heat							
kJ/kg	39 700	38 700	39 700	38 700	38 800	35 900	41 500
kcal/kg	9490	9250	9480	9250	9280	8600	9870
Moisture, %	0.42	0.35	0.45	0.57	0.47	0.71	0.43
Ash content, %	1.90	3.7	1.85	3.66	1.9	6.1	—
Effective viscosity, Pa·sec, at							
40 °C	0.036	1.41	0.032	1.18	0.126	—	0.004
80 °C	0.031	0.4	0.029	0.4	0.109	—	0.0031
Flash temperature, ^o C	110	125	110	125	107		90
Stability	Weakly stable	Stable	Weakly stable	Stable	Weakly stable	—	—

TABLE 1. Composition and Properties of the Composite Liquid Fuel Based on Products of Thermal Decomposition of Worn Tires

As to the qualitative indices, the CLF is analogous to heavy hydrocarbon fuels of the type of boiler oil M100 and can be used in liquid-fuel boilers both in the initial form and in a mixture with other liquid fuels. The composition and properties of the composite liquid fuel based on products of thermal decomposition of worn tires are presented in Table 1.

To prepare CLF, it is expedient to use a higher-boiling fraction $(>300^{\circ}C)$ with the addition of a water condensate.

From considerations of ecological safety of the technology of obtaining fuel from oil, it seems promising to obtain fuel by mixing three components: a condensate (of water), a liquid fraction (combustion heat of 43 MJ/kg), and a solid residual (combustion heat of 35 MJ/kg). The sulfur content in the fuel obtained is from 0.05 to 1.26 mass %.

Conclusions. Unlike the existing technologies that feature a high energy consumption and require complex equipment, thermolysis of organic waste in superheated steam permits obtaining alternative liquid fuel and technical carbon along with reclamation of various types of used tires. Moreover, the proposed technology and the developed apparatuses permit reclaiming, the together with technical rubber waste, various kinds of organic waste (waste of wood, plastics, solid garbage, waste of the chemical industry) with the aim of obtaining valuable chemical components.

NOTATION

 C_p , specific heat capacity of products, kJ/(kg·^oC); G, rate, kg/h; M, mass, kg; Q, quantity of heat, kJ; q, specific condensation heat, kJ/kg; r, specific heat of waste decomposition, kJ/kg; T, temperature, ^oC. Subscripts: h, heating; total, total quantity needed for decomposition of waste; c.w., cooling water; c.w.con, cooling water in condenser; c.w.sol, cooling water conveyed to solid products of thermolysis; w, waste; s, steam; com.p, gaseous combustion products; loss, loss; d, decomposition; sol, solid products of thermal processing; (t), thermolysis chamber; cool, cooling and condensation of steam-gas mixture; (pr), preheating chamber; s.g, steam-gas mixture; (1), at entrance; (2), at exit; (3), at release into the environment.

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