## STEAM THERMOLYSIS OF DISCARDED TIRES: TESTING AND ANALYSIS OF THE SPECIFIC FUEL CONSUMPTION WITH TAIL GAS BURNING, STEAM GENERATION, AND SECONDARY WASTE SLIME PROCESSING

V. A. Kalitko,<sup>a</sup> Morgan Chun Yao Wu,<sup>b</sup> V. A. Zhdanok,<sup>a</sup> and Benson Ching Tsai Yo<sup>b</sup>

This paper presents the process of steam thermolysis of shredded used tires for obtaining from them liquid fuel and technical carbon carried out in a screw reactor with heating due to the partial burning of obtained fuel and burning of the tail combustible gas. The features and advantages of using steam for safety and stability of the process, including the problem of secondary waste slime processing, have been considered. The specific fuel consumption and the steam generation per 1 kg of processed tires and, separately, the gas consumption for power supply (heating) of the process without using fuel, as well as with additional burning of fuel for processing slime together with tires, have been considered.

Keywords: waste, tires, processing, pyrolysis, fuel, carbon, steam, slime.

**Introduction.** Pyrolysis of used tires has been known in the world from many patents and scientific publications since the 1980s. In the last few years, more and more consideration has been given to the questions of ecological safety of this technology. For a general survey of the problem in China of today one can refer to both [1] and the brief analysis of the US patents on this topic of previous years [2]. The process is realized mainly by processing shredded tires in screw or drum reactors as evidenced by the recent US patents in this field ([3–8] and others).

At the sane time in Russia and Belarus a new approach to the reclamation of tire wastes was proposed [9–13], etc. The essence of this approach is that superheated steam is supplied directly into the reactor, providing additional heating and stabilizing the pyrolysis temperature. Moreover, the presence of steam makes the process less explosive [14], which is particularly important if we take into account that this method was first developed and used for processing whole tires in volume chamber reactors in which, to ensure safety, systems of sluices and intermediate chambers before and after the reactor are required.

The method of steam pyrolysis was used by us for processing shredded tires in a screw reactor at the industrial plant-factory "Land Join Ltd." (Taiwan) in 2007. The technological process and the factory equipment had been developed by the A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus (ITMO), where experimental studies of the vapor thermolysis of tires in chamber-type reactors were already conducted, in cooperation with the company "Enrestec Inc." (Taiwan). Pilot-production tests and the subsequent work of the factory have shown that optimizing the steam supply increases the output of the screw-type reactor and the efficiency of processing shredded tires in it. In 2007, this development was registered as a joint invention at the Intellectual Property Center of the Republic of Belarus. This paper presents some of the technical results of these tests and analytical calculations of the steam generation and the specific energy input per 1 kg of processed rubber, which may be of interest and useful for other researchers and specialists in this field.

**Description of the Process and Equipment.** The factory is designed as a complex of equipment consisting of two modules processing 1000 kg/h each. The main unit of the module is a screw reactor 1 (see Fig. 1) operating on the principle of two waste pipes located in the gas heating chamber 2 one above the other. The shredded material of tires is charged, transported, and pyrolized in the reactor along these pipes from which the pyrogas is carried into the fuel and steam condensers 3 and 4, respectively. The whole process proceeds under rarefaction of the gas fan 5

<sup>&</sup>lt;sup>a</sup>A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus; email: cpt@dnp.itmo.by; <sup>b</sup>Enrestec Inc., Gangshan, Kaoshiung County 820, Taiwan; email: morgan@enrestec.com. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 82, No. 2, pp. 242–251, March–April, 2009. Original article submitted March 13, 2008.



Fig. 1. Flow diagram (ITMO, National Academy of Sciences of Belarus and "Enrestec Ltd". (Taiwan)) for steam thermolysis of shredded tires in a screw reactor: 1) two-pipe screw reactor; 2) heating chamber of the reactor; 3) fuel condenser; 4) steam condenser; 5) tail gas fan; 6) steam boiler-recoverer; 7) coil-superheater of steam; 8) fuel condensate separator; 9) vessel-settler of steam condensate; 10) tail gas reburning furnace.

located at the outlet of the latter from the condensers. Steam is generated in the boiler-recoverer 6 by the heat of the furnace gases flowing out of the reactor heating chamber, and its mass ratio in the mixture with the pyrogas is about 1:2. Before supplying into the reactor the gas is superheated to a temperature no less than the pyrolysis temperature, which takes place in the coil pipe 7 arranged along and around the reactor. Upon condensation of the pyrogas and steam in 3 and 4 the fuel condensate is fed into the separator 8 and water is drained into the vessel 9, where it precipitates and is conveyed back into the steam boiler. The noncondensable tail gas is conveyed by the fan 5 into the furnace 10 where it is burned up together with a small quantity of fuel needed mainly to stabilize the gas combustion. The liquid-fuel burner sustaining the tail gas burning in the furnace operates at full power with the reactor preheated to the pyrolysis temperature. In so doing, the pyrogas pipelines and condensers are heated by the steam generated in the process of reactor heating. As soon as the required temperature is reached, charging of the reactor begins, and this process is carried out in two to three stages to avoid a decrease in the temperature upon starting the reactor. As the charging proceeds, the pyrogas yield increases to such an extent that the fuel burning can be terminated and the reactor will only be heated by the reburning tail gas. To discharge the carbon residual of pyrolysis, which in this case is considered as the main processing product and whose yield accounts for up to 35% of the charge (including up to 5% of the steel-wire cord remnants), we used a double sluice-gate system operating under a general evacuation of the reactor down to -0.5 kPa carried out by the fan 5. Then the carbon is powdered and the metal cord is separated by screening in a trommel screen with final cleaning in a magnetic separator.

Since the reactor operates under evacuation, providing its explosion-safety is particularly important and is achieved by limiting the access of air to the reactor from the charge and discharge sides. In particular, at the charge, this is provided by placing the pyrogas outlet pipe directly in the charging zone so that the possible inflow of air by-passes the reactor and the air together with the pyrogas flows only into the condensers where the thermal conditions for explosion are absent. At the discharge, explosion-safety is achieved due to the fact that steam is conveyed into the reactor from the discharge side, forming a kind of a steam screen preventing the access of air to the reactor. The charge bin hydrogate tested at the start of the operation was not used further, since it created 10–15% of humidity of the processed shredded material, which lowered by  $100-150^{\circ}$ C the yield temperature of pyrolysis products and, there-

fore, increased the energy input of the process. Practice has shown that operation without a hydrogate is also safe, but all explosion-safety standards for gas should be observed: the presence of a bypass of the gas pipeline for gas release into the atmosphere when the reactor is shut down (prevents explosive accumulation of the gas and its mixing with air in the furnace), a check valve of the gas near the furnace (prevents overshoot of the flame from the furnace along the pipeline), and an explosion valve for use in the event of a puff of the gas in the furnace and in the reactor heating chamber (provides release of the explosion pressure pulse into the atmosphere). Moreover, since the carbon discharge and screening trommel communicates with the reactor, it must be aired and the air outlet must be located adjacent to the charging opening of the trommel so that the possible gas inflow from the reactor is aired there and then without filling the trommel volume.

As a result of the pyrogas condensation, a liquid fuel is formed in the amount of 35–40% of the charged material. We tested two types of tube condensers and the choice was made in favor of scrubber-type condensers with water-cooling by siphon pipes in combination with evaporative injection of water for condensation temperature control. Tube condensers from dense tube bundles were simply clogged with slime from a sticky mixture of soot and fuel condensate, which was a consequence of the high content of carbon in the pyrogas (no less than 0.5% of the charge) which is carried away from the reactor in the process of rubber decomposition. In the presence of carbon particles in the pyrogas, on their developed dispersion surface there occurred, in the first place, condensation of the heavy oil fraction, and the particles coalesced and settled on the tubes in the form of oil slime. In so doing, on the cold surface of the tubes in the total composition of the fuel up to 25–30% of steam condenses and, to minimize the content of this water in the fuel, it is necessary to exclude tubes and use only evaporative injection decreasing thereby the initial supply of steam into the reactor. To upgrade the quality of the fuel condensate, one also has to minimize and optimize, wherever possible, the temperature conditions of pyrolysis in order to reduce carbonization of the process, i.e., the formation of carbon (pyrocarbon) particles in the pyrogas, otherwise carry-over of this carbon is practically unavoidable and leads to the formation of the above slime also in the fuel condensate.

Cleaning of impure fuel condensate from water and slime is carried out in a Laval separator 8. In so doing, the yield of combustible light liquid fuel amounts to 20-25% of the charge and the fuel itself retains its dark (brown) color. Heavy fuel oil fractions of the condensate remain in the water-carbon slime including up to 90% of water. This slime is subject to repeated processing together with the material of tires, which is specially considered below. If the fuel condensate is cleaned and separated by the flotation method, then the fuel oil fraction separates from the carbon precipitate and accounts for 15-20% of the total quantity of condensate.

It should be noted that the condensation and repeated generation of steam apparently do not increase the energy efficiency of the process compared to the usual pyrolysis without steam. However, since steam is generated on waste furnace gases and does not require additional fuel consumption, the carry-over of sooty carbon by the steam flow from the reactor can be considered as the only negative moment associated with the presence of steam in the given process. For example, when, on average, up to 250 kg/h of steam, i.e., up to 25% of the charge is supplied into the reactor, its quantity amounts up to 50% of the mass of the pyrogas formed, since the latter is also formed to the extent of 50% of the charge. At a high density of a pyrogas consisting at 350°C and above mainly of heavy hydrocarbons of the terpene series  $(C_5H_8)_{n=2,3,4...}$  its characteristic volume is insignificant and steam occupies up to 80-85% of the volume. This high volume content of steam in the composition of the steam-gas mixture just makes it the basic factor of the carry-over of carbon in the reactor. In particular, the flow rate of steam in the average free crosssection of the reactor was estimated by us to be within the limits of 4-5 m/sec, which is quite enough for the carryover of carbon particles of size up to 100 µm. The carry-over caused by the rotation of the reactor screw can be neglected, since this rate did not exceed 3-3.5 rpm. Under the operating conditions, we carried out tests for decreasing the supply of steam into the reactor with the aim of minimizing the carry-over of carbon with the preservation of the main functions of the steam as a stabilizer of the process. It has been found that when steam is supplied to the extent of up to 10% of the charge, a fairly high quality of the fuel condensate with an insignificant carbon carry-over and precipitate is provided, but this proved to be obviously insufficient for the thermal stability of the process.

Stability of pyrolysis means that the temperature of the pyrogas at the outlet from the reactor should be not lower than  $350^{\circ}$ C to prevent its condensation in the pipe. If the temperature drops to  $300^{\circ}$ C and below, then the pipe is clogged with a pasty mixture of soot and fuel oil condensate. However, already at  $450^{\circ}$ C and above there appears a disadvantage of such high-temperature pyrolysis. This disadvantage is that in the pyrogas composition the content of

light noncondensable hydrocarbons increases. This leads to a decrease in the yield of the liquid fuel condensate and, accordingly, to an increase by no less than 5% in the volume of the yield of the tail gas for reburning, which we estimated by the higher (by 100–150°C) reburning temperature. The quantity of the gas therewith increases for two reasons: first, due to the formation of more and more pyrogas and the increase in the yield of tail gas as the reactor is charged, and then with increasing temperature in the furnace, as mentioned above. Thus, a temperature of pyrogas and of the pyrolysis leaving the reactor of up to 400°C is preferable in the given process, and the question of its thermal stability reduces to the allowable deviation of this temperature by  $\pm 50^{\circ}$ C. It should be noted that the process temperature may also vary because of the charge inhomogeneity, and therefore the presence of steam markedly increases the thermal stability of the process due to the fact that the total mass and the heat capacity of the pyrogas together with the steam are approximately twice higher than those of the pyrogas taken separately. Consequently, all other things being equal, for steam thermolysis the possible variations in the process temperature are much less vivid.

Considering the thermal conditions of fuel condensation from the pyrogas in a mixture with steam, note that the dew point of the heavy (fuel oil) fractions of the fuel is lower, less than  $300^{\circ}$ C, whereas for industrial oil refining without steam it is higher and equals  $350-360^{\circ}$ C. Likewise, a decrease in the temperature of steam pyrolysis compared to the processes of similar processing of tires without steam [2–8], for which, in particular, according to the data of [8], a temperature of  $450-500^{\circ}$ C is preferable, is also observed. The carbon product thereby contains up to 3-4% of residual hydrocarbons whereas in the steam thermolysis the same quantity of carbon and higher (1–2% of the residue of hydrocarbons) is obtained at a process temperature of  $350-400^{\circ}$ C. It may be suggested that this is a result of the low partial pressure of the pyrogas in the reactor (0.15–0.2 bar) due to the high volume content of steam in it (80–85%) at a total pressure in the reactor and condensers close to atmospheric pressure. Considering the low partial pressure as a kind of pyrogas vacuum, to confirm this, one can refer to [15], where pyrolysis of tires was carried out with a vacuum pump evacuated to 0.07 bar and where a temperature of up to  $400^{\circ}$ C sufficed also for obtaining a carbon product with a low hydrocarbon residue.

The steam finally condenses at 40–45 $^{\circ}$ C in the column 4 and contains all condensable and water-soluble organic residues present in the pyrolysis products — phenols, benzenes, benzines, etc. The tail gas noncondensable at this temperature consists of lighter residues: butadiene, pentane, ethylene, propylene, methane, hydrogen, etc., including also the residual saturated content of the steam. According to the data of [8], the reduced combustion heat of such a tail gas in the usual pyrolysis of tires is about BTU/ft<sup>3</sup> (40 MJ/m<sup>3</sup>). For the steam process this value strongly depends on the condensation temperature of the steam determining its saturation and the residual content in the gas. In particular, according to the data of [13], the calorific value of the gas was estimated to be approximately twice lower (19 MJ/m<sup>3</sup>), since the content of saturated steam in it was about 50% lower. Thus, to provide the lowest temperature of the steam condensation and a higher quality of the reburned gas with a small residual content of steam, not a mixing-type condenser but a tubular-type one is needed. At the same time the steam and other light hydrocarbons in the tail gas composition continue to condense, as a rule, as the temperature in the gas pipe decreases, and, therefore, standard separation vessels-steam traps are required for draining such a condensate before burning.

As mentioned above, the steam condensate includes different residues of both water-soluble and insoluble light in color and weight organic compounds. Upon precipitation of the lightest (in weight) insoluble organic matter in the vessel 9 the steam condensate goes back into the boiler, where the dissolved organic matter evaporates again and is included in the composition of the steam for pyrolysis. At a total initial content of organic matter in the condensate of up to 10% upon precipitation fairly pure water of light-yellow color (because of the residue of the soluble organic matter) is observed. In the course of such a closed cycle of water supply, the steam in the boiler, then the pyrogas in the reactor, and finally the tail gas from the condenser become increasingly saturated with vapors of this organic matter, and its content in the steam condensate decreases. As a result, the cooling temperature of the steam condenser remains unaltered, and the tail gas yield from it increases by about 5–10%, which presents no problems for its reburning in the furnace. From the operational background of a steam boiler with such organic impurities of water it may be concluded that the only difference from the operation with pure water without impurities is that foam is formed in the boiler. The possible incorrect readings for the water level are easy to adjust by blowing-through and washing regularly the glass of the level gauge column.

Moreover, irrespective of the method of pyrolysis of tires, the pyrogas contains inorganic acidic compounds  $NO_x$ ,  $SO_x$ , etc., as well as some heavy metals entering into the composition of the rubber [2]. In steam thermolysis,

all these highly soluble impurities also accumulate in the steam condensate, which after about 500 h of operation was observed and showed up as a change in the acidic index of the condensate water from neutral to pH 6.5. This is due to the fact that the 100%-saturation of steam in the condenser forms droplet-aerosol fog which, as in the high-efficiency scrubber, absorbs well the above impurities from the gas. Therefore, to prevent acid erosion of the pipes and equipment in steam thermolysis, the same control and alkali chemical treatment of water in the boiler as in the scrubber for cleaning waste furnace gases are required.

**Specific Steam Generation and Fuel Composition.** Burning of fuel is needed mainly at the beginning of the process for reactor preheating, steam generation, and heating with this steam the remaining equipment (pipes, fuel condenser, etc). Charging and pyrolysis of the material of tires are accompanied by a release of the tail combustible gas which is reburned, and thus the fuel consumption can be markedly decreased and even reduced to zero, which is considered below. Since the yield of this gas makes up a certain percentage of the charge mass (about 10%) and the steam for pyrolysis is generated by the heat of the furnace gases upon reactor heating, we can formulate analytically and determine the specific steam generation and the fuel consumption per 1 kg of the processed material in the form of the function of the main parameters of the process. Taking into account that up to 3-5% of the heat is released into the environment at a thermal efficiency of the furnace  $E_f = 0.95-0.97$ , the thermal load of the reactor in burning the fuel and the gas in the furnace can be written in the general form as

$$Q_{\rm r} = \left( G_{\rm oil} Q_{\rm oil} + \frac{\rm GAS}{100} G_{\rm t} Q_{\rm gas} \right) E_{\rm f} \,. \tag{1}$$

The pyrolysis is considered as a process of heating to a given temperature and further as a thermal destruction of the rubber at the same constant temperature, for which the quantity of the required heat is formulated as follows:

$$Q_{t} = G_{t} \left( c_{pt} \left( T_{p} - T_{a} \right) + h_{t} \right).$$
<sup>(2)</sup>

The superheating of the steam to the pyrolysis temperature in the coil pipe along and around the reactor is defined in the conventional way:

$$Q_{\rm ss} = G_{\rm s} c_{\rm ps} \left( T_{\rm p} - T_{\rm s} \right) \,. \tag{3}$$

Processes (2) and (3) proceed in the reactor heating chamber, whose thermal efficiency can be expressed in terms of the ratio between the gas flow enthalpy before the heating  $Q_{g1} = c_{pg}G_g(T_{g1} - T_a)$  and after it  $Q_{g2} = c_{pg}G_g(T_{g1} - T_{g2})$ , simplifying and obtaining this quantity in the form of the ratio between the corresponding temperatures alone:

$$E_{\rm r} = \frac{Q_{\rm g1}}{Q_{\rm g2}} = \frac{T_{\rm g1} - T_{\rm g2}}{T_{\rm g1} - T_{\rm a}}.$$
(4)

The heat flow from the furnace according to (1) is used for (2) and (3) with the reactor efficiency according to (4), and the specific fuel consumption per 1 kg of processed tires is determined from the total heat balance of the furnace and the reactor by substituting (1)–(4)

$$E_{\rm r}Q_{\rm r} = Q_{\rm t} + Q_{\rm ss} \,, \tag{5}$$

$$X = \frac{G_{\text{oil}}}{G_{\text{t}}} = \frac{c_{p\text{t}} (T_{\text{p}} - T_{\text{a}}) + h_{\text{t}} + c_{p\text{s}} (T_{\text{p}} - T_{\text{s}}) \frac{G_{\text{s}}}{G_{\text{t}}}}{Q_{\text{oil}} E_{\text{r}} E_{\text{f}}} - \frac{\text{GAS}}{100} \frac{Q_{\text{gas}}}{Q_{\text{oil}}},$$
(6)

from which for the subsequent solution the specific steam generation per 1 kg of tires is also formed:

$$Y = \frac{G_{\rm s}}{G_{\rm t}} = \frac{G_{\rm s}}{G_{\rm oil}} \frac{G_{\rm oil}}{G_{\rm t}} = X \frac{G_{\rm s}}{G_{\rm oil}}.$$
(7)

In so doing, the steam generation is determined by the heat balance of the boiler:

$$Q_{\rm s} = G_{\rm g} c_{pg} \left( T_{\rm g2} - T_{\rm g3} \right) = G_{\rm s} \left( c_{pw} \left( T_{\rm s} - T_{\rm a} \right) + h_{\rm s} \right) \,. \tag{8}$$

The furnace gas flow has three components: the first and the second ones — from burning the fuel and the tail gas which are characterized approximately as follows:  $g_a = 15-16 \text{ kg/kg}$  — the known stoichiometric air supply per 1 kg of hydrocarbon fuels;  $\alpha_1 = 1.3-1.35$  — the conventional excess coefficient of air for liquid fuel combustion;  $\alpha_2 = 1.05-1.1$  — same, for gas combustion. A series of simple substitutions in the form  $G_{g1,2} = G_{oil}g_a\alpha_1 + G_{gas}g_a\alpha_2 = G_{oil}g_a\left(\alpha_1 + \alpha_2 \frac{G_{gas}}{G_{oil}}\right)$  and  $\frac{G_{gas}}{G_{oil}} = \frac{GAS}{100} - \frac{G_t}{G_{oil}} = \frac{GAS}{100} - \frac{1}{X}$  yields for them the following expression:

$$G_{g1,2} = G_{oil}g_a \left( \alpha_1 + \alpha_2 \frac{\text{GAS}}{100} \frac{1}{X} \right).$$
(9)

The third component is the inflow of air from the outside, which is required to decrease the temperature of gases before the reactor to  $T_{g1} = 850-900^{\circ}$ C, whereas the working temperature in the furnace should be high enough,  $T_{f} = 1100 \pm 50^{\circ}$ C, in order to provide complete reburning of all components of the tail gas. By the mixing heat balance method this is formulated as follows:  $G_{g1,2}c_{pg}(T_{f} - T_{g1}) = G_{a}c_{pa}(T_{g1} - T_{a})$ , where the heat capacities of air and air-diluted furnace gases can be assumed to be approximately equal:  $c_{pg} \approx c_{pa}$ . At the given temperatures the relation between the air inflow and the flow of combustion products from the furnace is characterized by a quite definite value approximately as  $\frac{G_{a}}{G_{g1,2}} = \frac{T_{f} - T_{g1}}{T_{g1} - T_{a}} \approx 35\%$ . As a result, the total flow of furnace gases in the reactor heating chamber is

$$G_{\rm g} = G_{\rm g1,2} + G_{\rm a} \cong 1.35G_{\rm g1,2} \,. \tag{10}$$

Both air excess coefficients can simply be multiplied by 1.35 and reduced to the form  $\alpha_f = 1.75-1.85$  and  $\alpha_2 = 1.45-1.5$  in order to use further only (9), having included in it also the free air inflow according to (10). In so doing, we obtain the first result from (7)–(9) followed by the solution for *Y*:

$$Y = \frac{G_{\rm s}}{G_{\rm t}} = \frac{c_{pg} \left(T_{g2} - T_3\right) g_{\rm a}}{c_{pw} \left(T_{\rm s} - T_{\rm a}\right) + h_{\rm s}} \left(\alpha_1 X + \alpha_2 \frac{\rm GAS}{100}\right).$$
(11)

The final solution is obtained by substituting (7) into (11) for X:

$$X = \frac{c_{pt} (T_{p} - T_{a}) + h_{t} - \left(Q_{gas}E_{r}E_{f} - \alpha_{2}c_{ps} (T_{p} - T_{s})\frac{c_{pg} (T_{g2} - T_{g3}) g_{a}}{c_{pw} (T_{s} - T_{a}) + h_{s}}\right)\frac{GAS}{100}}{Q_{oil}E_{r}E_{f} - \alpha_{1}c_{ps} (T_{p} - T_{s})\frac{c_{pg} (T_{g2} - T_{g3}) g_{a}}{c_{pw} (T_{s} - T_{a}) + h_{s}}}.$$
(12)

Having included the process parameters in the corresponding complexes:  $q_t = c_{pt}(T_p - T_a) + h_t$  — the specific heat of pyrolysis of 1 kg of tires,  $q_s = c_{pw}(T_s - T_a) + h_s$  — the heat for the generation of 1 kg of steam,  $q_{ss} = c_{ps}(T_p - T_s)$  — the heat of superheating 1 kg of steam for pyrolysis,  $q_g = c_{pg}(T_{g2} - T_g3)$  — the heat transfer of 1 kg of furnace gases in the steam boiler-recoverer, and having combined these complexes in the form of the simplex

$T_{g1}$ , °C	T <sub>g2</sub> , <sup>o</sup> C	<i>T</i> <sub>g3</sub> , <sup>o</sup> C	<i>T</i> <sub>g4</sub> , <sup>o</sup> C	S, mm	GAS, %									
					6		7		8		9		10	
					X	Y	X	Y	X	Y	X	Y	X	Y
850	450	650	350	5	0.00896	0.164	0.00026	0.162		0.156				
900	500	700	400	10	0.0199	0.236	0.0111	0.232	0.0024	0.229		0.226		
950	550	750	450	15	0.0333	0.330	0.0245	0.326	0.0157	0.322	0.0069	0.318		0.314

TABLE 1. Specific Fuel Consumption X (kg/kg) and Steam Generation Y (kg/kg) as Calculated Functions of the Low-, Medium-, and High-Temperature Regimes of Pyrolysis of Shredded Tires

TABLE 2. Specific Fuel Consumption X (kg/kg) and Steam Generation Y (kg/kg) as Calculated Functions of the Low, Medium, and High Steam Pressure and a Low Thermolysis Temperature of 350°C

$T_{\rm s}$ , <sup>o</sup> C	ð, bar	GAS, %											
		6		7		8		9		10			
		X	Y	X	Y	X	Y	X	Y	X	Y		
$120 \pm 2.5$	1	0.0351	0.335	0.263	0.331	0.0176	0.327	0.0088	0.323		0.319		
$140 \pm 2.5$	3	0.0337	0.319	0.0250	0.369	0.0162	0.312	0.0075	0.308		0.304		
$160 \pm 2.5$	5	0.0325	0.304	0.0238	0.301	0.0150	0.297	0.0063	0.294		0.291		

 $A = q_{ss} \frac{q_g g_a}{q_s}$  characteristic of the given process, results (11) and (12) can be given in a more compact and convenient

(for calculations) form

$$X = \frac{G_{\text{oil}}}{G_{\text{t}}} = \frac{q_{\text{t}} - (Q_{\text{gas}}E_{\text{r}}E_{\text{f}} - \alpha_2 A)\frac{\text{GAS}}{100}}{Q_{\text{oil}}E_{\text{t}}E_{\text{f}} - \alpha_1 A},$$
(13)

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$$Y = \frac{G_{\rm s}}{G_{\rm t}} = \frac{q_{\rm g}}{q_{\rm s}} \left( \alpha_1 X + \alpha_2 \frac{\rm GAS}{100} \right). \tag{14}$$

The question is to what extent the yield and reburning of the tail gas with respect to the charge of the reactor will be sufficient for its heating without fuel, which can easily be determined from (13) at X = 0:

$$GAS_{max} = \frac{q_t}{Q_{gas}E_rE_f - \alpha_2 A}$$
(15)

and calculated for the above parameters as approximately  $GAS_{max} \cong 10\%$ .

Computational Modeling of the Process for the Fuel Consumption and Steam Generation. The above results obtained in the form (13)-(15) are based on the heat balance equations and, therefore, do not contain such a parameter as the pyrolysis time depending not only on the temperature but also on the size of shreds of tires. In this connection, it may be observed that the tests were carried out in the  $350-450^{\circ}$ C range at the same temperature of the steam-gas mixture at the exit from the reactor which was heated by the furnace gases in the 850–950°C range at the entrance to the chamber. Tests were carried out under constant-load conditions from 500 to 1000 kg/h of shredded tires whose fragments of size 50-100 mm and thickness 5-15 mm were transported along the reactor length by the screw at a rate of 3-3.5 rpm for 12-13 min.

The heat balance of the process was provided by burning up to 70 kg/h of the fuel in the furnace, which is required mainly in preheating the reactor and the equipment on the whole. As soon as the given temperature was reached, initial loading of the reactor approximately up to 50% of its output was carried out and the burner automatically switched to its minimum for fuel of approximately up to 30 kg/h, since with the beginning of pyrolysis and pyrogas formation in the reactor the tail gas is reburned in the furnace. As the charge is increased to 100%, the yield of the gas for reburning increases and, accordingly, the burner is switched off as a rule. Assuming, according to the data of [4–8], the gas combustion heat of about 40 MJ/kg and the gas yield of up to 10% of the charge mass, it may be concluded that the tail gas becomes sufficient for the further heating of the reactor. This is in good agreement with the computational modeling of the process according to (13) and (14) presented in Table 1.

No considerable dependence of the process on the initial temperature (pressure) of the steam is presumed since in any case the steam is superheated to the pyrolysis temperature. And the reactor pressure therewith will be held close to atmospheric or with an insignificant evacuation to 0.005 bar, which is provided by an adequate fan. The steam pressure in the boiler is needed only for overcoming the hydraulic resistance of the steam coil-superheater, and the computational modeling by (13) and (14) gives a slight difference between the results for different initial temperatures (pressures) of the steam, as is shown in Table 2.

**Processing of Secondary Waste Slime.** As mentioned above, in the given steam process the problem of the water carbon-fuel oil slime remaining after the fuel separation from the steam condensate arises. If this slime is again separated from the water, then it can be used in asphalt for pavement, as is done at the plant in Taiwan. In the absence of markets, the slime can be processed by the same pyrolysis technique by mixing it proportionately with the reactor charge material. The slime humidity is up to w = 90% and, to simplify the analysis, it may be considered as only consisting of water. In so doing, the fuel consumption, according to (13), increases including the additional expenditure of heat in the form of the following calculation complexes:  $q_{\rm W} = wc_{p\rm W}(100 - T_{\rm a} + h_{\rm s})$  — the heat of moisture evaporation from 1 kg of slime at  $100^{\circ}$ C,  $q_{\rm WW} = wc_{p\rm s}(T_{\rm p} - T_{\rm s})$  — the heat of the subsequent heating of the steam from 1 kg of slime to the pyrolysis temperature,  $q_{\rm W} + q_{\rm WW} = wB$  — the total heat of the pyrolysis processing of 1 kg of slime, where for abbreviation one more simplex  $B = c_{p\rm W}(100 - T_{\rm a}) + h_{\rm s} + c_{p\rm s}(T_{\rm p} - 100)$  is used. According to (13), the higher fuel consumption per 1 kg of charged tires is formulated as the sum

$$X_{\rm w} = \frac{q_{\rm t} - (Q_{\rm gas}E_{\rm r}E_{\rm f} - \alpha_2 A)\frac{\rm GAS}{100} + wB\frac{\rm SLU}{100}}{Q_{\rm oil}E_{\rm r}E_{\rm f} - \alpha_1 A} = X + \frac{wB\frac{\rm SLU}{100}}{Q_{\rm oil}E_{\rm r}E_{\rm f} - \alpha_1 A},$$
(16)

whence the very increase in the fuel consumption with respect to its normal value for the heating process according to (13) without slime equals

$$\Delta X = \frac{wB \frac{\text{SLU}}{100}}{Q_{\text{oil}}E_{\text{r}}E_{\text{f}} - \alpha_{1}A},$$
(17)

$$\frac{\Delta X}{X} = 1 - \frac{wB \frac{\text{SLU}}{100}}{q_{\text{t}} - (Q_{\text{gas}}E_{\text{r}}E_{\text{f}} - \alpha_{2}A)\frac{\text{GAS}}{100}}.$$
(18)

The fuel consumption for the slime processing should not exceed the maximum working heat load of the reactor with tail gas reburning up to GAS<sub>max</sub> = 10% assuming thereby the highest temperature of the heating gases  $T_{g1} = 950^{\circ}$ C at a minimum pyrolysis temperature  $T_{p} = 350^{\circ}$ C and the following parameters of the thermal efficiency of the process:  $q_{t} = 1.186$  MJ/kg — the calculated heat of pyrolysis of 1 kg of tires at the above temperature;  $q = \frac{GAS}{100}Q_{gas} = 0.1.40 = 4.0$  MJ/kg — the heat of reburning 10% of the tail gas per 1 kg of pyrolysis,  $E_{min,r} = \frac{q_{t}}{q} = \frac{1.186}{4.0} = 30\%$  — the minimal thermal efficiency of the reactor at  $350^{\circ}$ C,  $E_{max,r} = \frac{T_{g1} - T_{g2}}{T_{g1} - T_{a}} = \frac{950 - 550}{950 - 25} = 43\%$ 

same, at a maximum heating temperature of 950°C.

The heat power reserve for slime processing is defined as the ratio of the fuel required for this purpose to the fuel consumption without slime:

$$\frac{\Delta X}{X} = E_{\max,r} - E_{\min,r} = 13\%$$
 (19)

Substituting (13) into (18) and (19) yields:

$$SLU_{\min} = \left(E_{\max,r} - E_{\min,r}\right) \frac{\left(Q_{gas}E_{r}E_{f} - \alpha_{2}A\right)\frac{GAS}{100}}{wB},$$
(20)

whence by calculating the above parameters we get:  $SLU_{min} \cong 6\%$ .

Conclusions. On the basis of the present development and the tests carried out it may be concluded that the screw reactor with a coil steam superheater is an effective design for processing shreds of tires by the method of steam thermolysis whose fire proofness and nonexplosiveness are provided by the correct organization of the heat supply to the reactor and the removal from it of the steam-gas mixture. The ecologically safe and economical proceeding of the process is provided by the closed system of obtaining and using steam for such thermolysis, as well as by the complete reburning of the tail gas for heating, including also the dual mechanism of scrubbing the gases in both the scrubber and the condenser. Because of the high specific charge of the reactor volume, the specificity of the process is the formation of a larger number of soot (pyrocarbon) particles and their carry-over with steam, which impedes the pyrogas condensation into liquid fuel, requires for this purpose special methods and condenser designs, and leads to the formation of secondary wastes in the form of carbon-fuel oil slime upon fuel separation. Slime can be marketed for adding it to asphalt or it can also be pyrolyzed by means of proportional mixing with the material of tires, and the carry-over of carbon as the main reason for the slime formation can be decreased by optimizing the steam supply and the geometry of the reactor itself. The given technology of steam thermolysis permits using the standard boilersrecoverers for closed steam generation from the circulating water of the process admitting the presence in it of residual organic and inorganic compounds entering into the composition of the tire rubber and by fulfilling the standard requirements on the quality control and chemical treatment of water for both the boilers (hardness of water) and the scrubbers (acidity). The principal scientific-practical results of the tests are as follows:

1. Independent generation of steam from waste furnace gases to the extent of 25-30% of the reactor charge suffices to maintain the nonexplosiveness and thermal stability of the process. The presence of steam thereby permits decreasing the pyrolysis temperature to  $350-400^{\circ}$ C at a high quality of the carbon product in the form of 1-2% of the residual content of hydrocarbons. At the same time the above consumption of steam is excessive for the free space of a reactor of diameter 0.6 m and creates in it a carry-over of the sooty carbon in the pyrogas composition which fouls the condenser and worsens its operation, as well as requires additional separation cleaning of the fuel condensate. In this connection, it is necessary to optimize the generation and supply of steam as applied to the sizes of the reactor and its charge.

2. Steam pyrolysis of 1000 kg/h of shredded tires with sizes and thickness of fragments within the limits of 50–100 mm and 5–15 mm, respectively, requires up to 13 min of the material residence time in a screw reactor at a temperature of  $350-450^{\circ}$ C, for whose heating a temperature of the furnace gases of  $850-950^{\circ}$ C suffices, which can be fully provided by reburning the tail gas, whose yield constitutes 10% of the charge mass.

3. In working with water-tube condensers, the fuel product includes 25–30% of moisture of the partial condensation of steam on the cold surface of tubes, which requires subsequent separation of the fuel from this moisture. The carry-over of carbon in the pyrogas and the presence of its precipitate in the fuel upon separation lead to the formation of fuel foil-water slime of humidity up to 90%, and the possibility of its secondary processing together with the pyrolysis of shredded tires has been estimated to amount to 6% of the mass of charged tires.

## NOTATION

 $c_{pt}$ ,  $c_{ps}$ ,  $c_{pw}$ ,  $c_{pg}$ ,  $c_{pa}$ , heat capacity of tire rubber, steam, water, flue gases, and air, respectively, J/(kg·<sup>o</sup>C);  $E_{f}$ ,  $E_{r}$ , thermal efficiency of the furnace and the reactor, respectively; GAS, yield of reburned tail gas with respect to the reactor load, %;  $G_{t}$ ,  $G_{s}$ ,  $G_{oil}$ ,  $G_{g}$ , charging of tires, steam generation, consumption of fuel and flue gases in the heating chamber of the reactor, respectively, kg/h;  $G_{gas}$ , consumption of reburned tail gas, kg/h;  $G_{g1,2}$ , consumption

of flue gases in burning the fuel and tail gases, respectively, kg/h;  $G_a$ , inflow of air to the flue gases, kg/h;  $g_a = 15-16$  kg/kg, stoichiometric consumption of air for combustion of 1 kg of hydrocarbon fuels;  $h_t = 640$  kJ/kg, heat of the thermal destruction of 1 kg of rubber in pyrolysis;  $h_s$ , specific heat of steam generation, J/kg; p, steam pressure, bar;  $Q_s$ , heat power of the steam generation in pyrolysis of tires, MJ;  $Q_{ss}$ , heat power of the steam superheating to the pyrolysis temperature, MJ;  $Q_t$  heat power of the pyrolysis proper, MJ;  $Q_r$ , total heat power of the reactor, MJ;  $Q_{oil}$ ,  $Q_{gas}$ , specific combustion heat of the fuel and the tail gas, respectively, MJ/kg; s, material thickness, mm; SLU, processing of slime wastes with respect to the mass of charged tires, %;  $T_{g1}$ ,  $T_{g2}$ ,  $T_{g3}$ , temperatures of flue gases at the entrance to the reactor heating chamber, at the exit from the chamber, and further at the exit from the steam boiler, respectively, <sup>o</sup>C;  $T_p$ , pyrolysis temperature, <sup>o</sup>C; w, humidity of carbon-fuel oil slime wastes, %; X, specific consumption of liquid fuel per 1 kg of charged tires;  $\alpha_1 = 1.75-1.85$ ,  $\alpha_2 = 1.45-1.5$ , air excess coefficients in burning liquid fuel and gas, respectively, increased by a factor of 1.35 for taking into account the free air inflow into the reactor heating chamber. Subscripts: a, air; f, furnace; g, furnace gases; gas, tail gas; max, maximum; min, minimum; m, mean; oil, liquid fuel; p, pyrolysis; r, reactor; s, steam; ss, superheated steam; t, shredded tires; w, water.

## REFERENCES

- 1. Yang Yongrong, Chen Jizhong, and Zhao Guibin, Technical advance on the tire pyrolysis of used tires in China, Proc. China-Japan Int. Academic Symp.: Environmental Problem in Chinese Iron-Steel Making Industries and Effective Technology Transfer, Sendai, Japan, 6 March (2000).
- 2. Patent U.S. 5735948 (1998). Process for Recycling Tires and Oils.
- 3. Patent U.S. 5705035 (1998). Tire Liquefying Process Reactor Discharge System and Method.
- 4. Patent U.S. 5720232 (1998). Method and Apparatus for Recovering Constituents from Discarded Tires.
- 5. Patent U.S. 5894012 (1999). Method and System for Recovering Marketable and Products from Waste Rubber.
- 6. Patent U.S. 6221329 B1 (2001). Pyrolysis Process for Reclaiming Desirable Materials from Vehicle Tires.
- Patent U.S. 6657095 B1 (2003). Continuous Temperature Variance Pyrolysis for Extracting Products from Tire Chips.
- 8. Patent U.S. 6736940 B2 (2004). Process for Pyrolizing Tire Shreds and Tire Pyrolysis Systems.
- 9. D. V. Aristarkhov and G. I. Zhuravskii, Modeling of the steam thermolysis of rubber waste, *Inzh.-Fiz. Zh.*, 74, No. 6, 146–151 (2001).
- 10. D. V. Aristarkhov, G. I. Zhuravskii, É. P. Polesskii, and B. A. Permyakov, Technologies of biomass, technical rubber, and plastic waste processing, *Inzh.-Fiz. Zh.*, **74**, No. 6, 152–155 (2001).
- 11. G. I. Zhuravskii and V. A. Sychevskii, Calculation of the thermolysis of used rubber tires, in: O. G. Martynenko (Ed.), *Heat- and Mass Transfer* [in Russian], Collected scien. papers, Minsk (2002), pp. 13–20.
- G. I. Zhuravskii and V. A. Sychevskii, Numerical calculation of the steam thermolysis of organic wastes, *Inzh.-Fiz. Zh.*, 76, No. 6, 104–109 (2003).
- 13. G. I. Zhuravskii, A. S. Matveichuk, and P. L. Falyushin, Obtaining fuels based on steam thermolysis, products of organic-waste, *Inzh.-Fiz. Zh.*, **78**, No. 4, 58–62 (2005).
- V. A. Kalitko, Steam-thermal processing of used tires: calculation of the rate of explosion-proof feed of steam, *Inzh.-Fiz. Zh.*, 81, No. 4, 750–754 (2008).
- 15. Patent U.S. 4250158 (1981). Process for Recovering Carbon Black and Hydrocarbons from Used Tires.