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PYROLYSIS OF SOLID POLYMER WASTE AND PROPERTIES OF OBTAINED PRODUCTS

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Pyrolysis of solid polymer waste (car tires) was investigated in the temperature range of 350–650°C for 15–105 minutes. It was established that the maximum yield of a liquid product (58%) was observed in the temperature range of 520–540°C. The obtained pyrocondensate was compared with oil and it was stated that pyrolysis condensate was quite heavy, but had low kinematic viscosity and average molecular weight. It was determined that the most part of sulfur (1.27–2.1%) remained in the solid residue during the rubber pyrolysis. Unsaturated hydrocarbons (12.9%) in pyrolysis oil were found due to the presence of double bonds in rubber and the formation of double bonds during the polymer destruction. It was found that increasing the pyrolysis temperature from 400 to 600°C led to a decrease in polycyclic naphthalenes and an increase in the proportion of aromatic ring in the molecule due to the cleavage of alkyl substituents. The fractional composition of pyrolysis products obtained in the temperature range of 520–540°C was determined. The yield of the gasoline fraction, the diesel fraction and the residue was 26–28 wt.%, 18–23 wt.% and 45–47 wt.%, respectively. Comparison of the properties of fractions obtained from pyrocondensate with traditional petroleum products showed that the content of sulfur compounds for gasoline and diesel fractions was overestimated due to the presence of sulfur vulcanizing agent in rubber. The content of aromatic compounds, density and viscosity were slightly increased in those fractions. The properties of the fraction 350°C (end of boiling) were almost the same as those of fuel oil.

Keywords: car tire, pyrolysis, fuel, dangerous substance, environmental problem, pyrocondensate, utilization.

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Introduction

Every year the amount of household waste in the industrialized countries of the world increases by an average of 2% [1,2]. Among the solid household waste, a significant share is occupied by spent car tires, which are a powerful source of environmental pollution and belong to the fourth class of danger. Waste of this type accumulated in landfills decomposes under natural conditions for at least 100 years. Under the influence of natural factors, dangerous toxic substances are released from rubber products: decomposition products of rubbers (monomers), carcinogens, namely carbon disulfide, formaldehyde and phenols. This causes a

deterioration of the ecological situation in the country, as well as the deterioration of the general health of the population and the formation of serious diseases [3].

That is why in recent years in many countries more and more attention is paid to solid waste processing methods that allow producing heat, electricity and secondary raw materials [4], which is a cost-effective and environmentally safer measure than uncontrolled storage in the environment [5,6].

It is known that waste rubber is processed to obtain a regenerate, which is used as a partial replacement of rubber in the manufacture of rubber products. However, the use of a regenerate in large



quantities is possible only in irresponsible rubber products (carpeting, bumpers, blocks at railway crossings, rubber bricks for sidewalks, lying cops, etc.).

A promising way to dispose of such waste is pyrolysis, which allows producing valuable raw materials for the chemical industry in the form of pyrolysis gas, liquid hydrocarbons, and a solid residue from which one can get a good carbon sorbent or carbon black [7].

The purpose of this work is to consider the feasibility of processing and disposal of solid polymer waste (spent car tires) by pyrolysis to prepare products suitable for the use as fuel components.

Experimental

The test was performed on cleaned and crushed side of the car tire (165/70 R13 79T), with the sizes of 5×5×5 mm with the weight of 50 g. The feedstock was loaded into a reactor and subjected to pelletization at 400°C, 450°C, 500°C, 550°C and 600°C for 30 min, 60 min and 90 min.

The installation (Fig. 1) consisted of a tubular reactor 2 with external heating 1, a condenser with water cooling 3, a container for receiving products 4, a gas meter to determine the amount of gas formed 5 and a manometer 6.

The decomposition products resulting from the pyrolysis were condensed and collected in the container, and the non-condensed gas was supplied to the gas meter. The structure-group composition and sulfur content of the obtained liquid products were determined by the n-d-M method (the state standard GOST 2059).

The content of volatile substances (the state standard GOST 6382), ash content (the state standard GOST 11022), and sulfur content (the state standard GOST 2059) were determined in the solid residue. The pyrolysis condensate obtained under the conditions of the maximum yield was divided into fractions: the beginning of boiling 180°C, 180–350°C

and the residue (350°C – the end of boiling). The fractional composition (the state standard GOST 2177), density (the state standard DSTU EN ISO 3675), kinematic viscosity (the state standard DSTU GOST 33), mass fraction of sulfur (the state standard GOST 2059 (ISO 351)), ash content (the state standard DSTU EN ISO 6245), mass fraction (the state standard GOST 9), content of aromatic hydrocarbons (the state standard GOST 6994), corrosion on the copper plate (the state standard DSTU EN ISO 2160), water-soluble acids and alkali content of the obtained fractions (the state standard GOST 6307) were determined.

Results and discussion

The results of pyrolysis at the temperatures of 400°C, 450°C, 500°C, 550°C and 600°C showed the need to evaluate the characteristics of the process in a wider temperature range. For this purpose, additional experiments were performed at temperatures of 350°C and 650°C for 60 minutes. The research results showed that the yield of liquid products does not change in the temperature range of 350–400°C, and it even decreases in the temperature range of 600–650°C due to their further pyrolysis (Fig. 2,a, curve 2). Therefore, for the duration of 30 and 90 min, the pyrolysis process was carried out in the temperature range of 400–600°C.

Experimental data show that the yield of a liquid product increases when the pyrolysis temperature rises to 520–540°C (Fig. 2,a); a further increase in the temperature leads to an increase in the gas formation (Fig. 2,b), and the yield of a solid product remains virtually unchanged (Fig. 2,c).

It can be seen from Fig. 3 that the yield of the volatile solids of the rubber pyrolysis is significantly reduced as the pyrolysis temperature increases. Furthermore, there are practically no volatile substances in the solid residues obtained at the temperature above 520°C.

Thus, the temperature of 520–540°C is

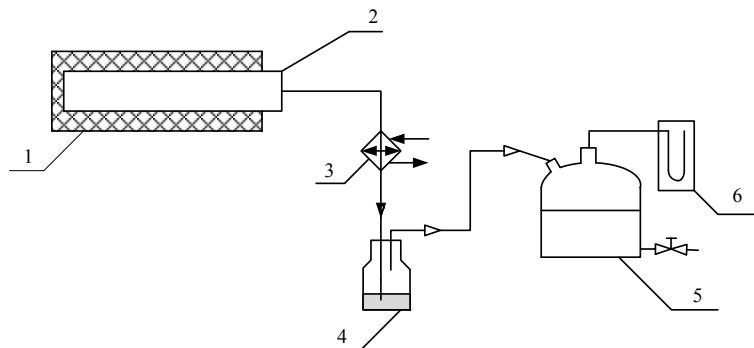


Fig. 1. Laboratory installation of pyrolysis of car tires: 1 – furnace; 2 – tubular reactor; 3 – condenser; 4 – container for collecting pyrolysis products; 5 – gas meter; 6 – pressure gauge

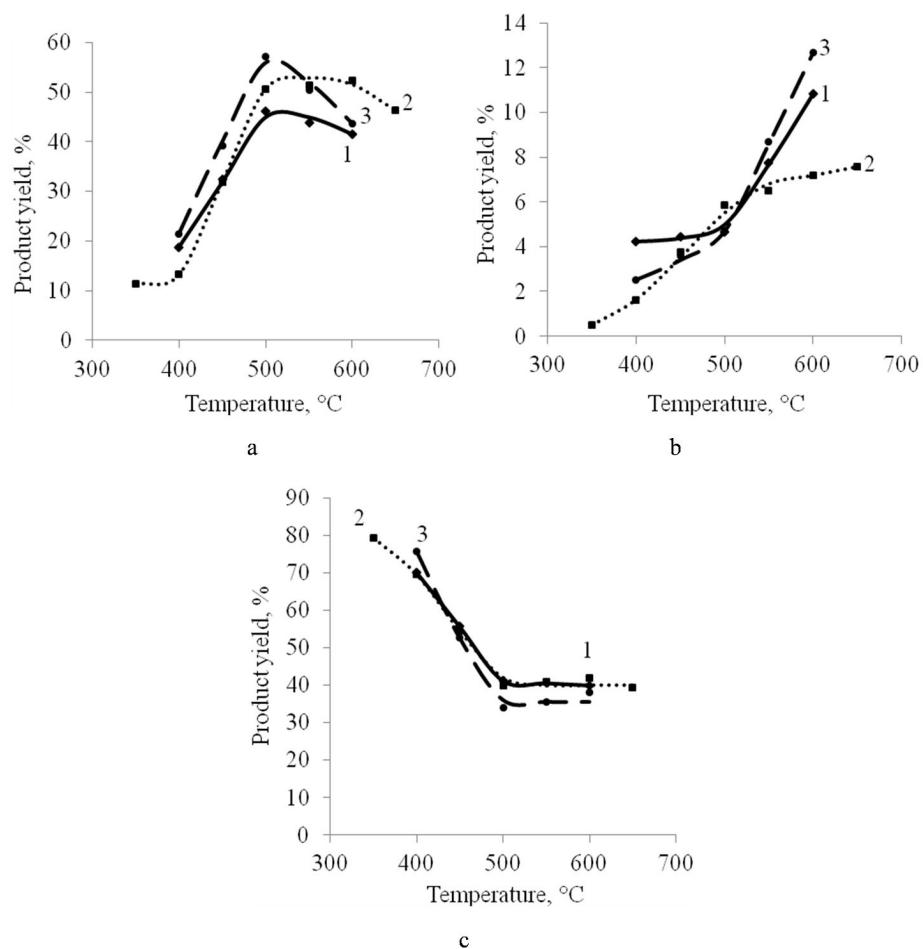


Fig. 2. Dependences of the pyrolysis products yield on the process temperature at different time periods: a – the yield of liquid products; b – the yield of gas; c – the yield of solid residue; 1 – at 30 min; 2 – at 60 min; 3 – at 90 min

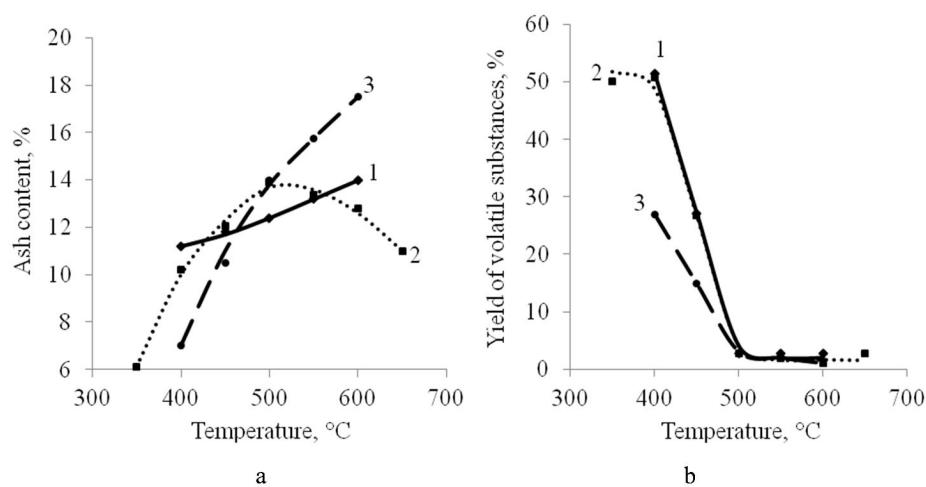


Fig. 3. Dependence of the ash content (a) and the yield of volatile substances (b) in the solid residue on the pyrolysis temperature at different time periods: 1 – at 30 min; 2 – at 60 min; 3 – at 90 min

sufficient for the complete pyrolysis of the rubber.

In these studies, pyrolysis occurred quickly and time did not significantly affect the process when the reactor was low-loaded (50 g of rubber). As the load mass is increased, the pyrolysis time will increase so that the entire mass will warm up and undergo full pyrolysis.

When comparing pyrolysis condensate with oil (Table 1), it can be seen that the pyrolysis product is quite heavy compared to oil, but it has low kinematic viscosity and average molecular mass. The disadvantage of pyrolysis oil is considered to be a sufficiently high content of sulfur compounds. According to this indicator, the products of rubber pyrolysis are no worse than only Orov, Lelyakivsk, Kachan and Hlynko-Rosbyshev oil. It should be noted, however, that the most part of sulfur remains in the solid residue (1.27–2.10%) during the rubber pyrolysis. Unsaturated hydrocarbons in pyrolysis oil are found due to the presence of double bonds in rubber and the formation of double bonds during the polymer destruction.

The study of the structural-group composition of pyrolysis oil depending on the temperature of the process (Table 2) showed that the total amount of carbon of the ringed structure of the product decreases (C_t) when the temperature of pyrolysis increases. The content of carbon in aromatic structures is increased (C_{ar}), i.e. the total number of ringed structures is reduced by the content of naphthenic compounds. As the pyrolysis temperature increases, the carbon content of alkyl substituents and paraffin hydrocarbons (C_p) increases.

It should also be noted that, on average, the total number of rings in the molecule is miniaturized as the process temperature increases (R_t). The

number of naphthenic rings in the molecule decreases from 1.56 to 0 (R_n), and the number of aromatic rings in the molecule increases from 0.25 to 1.05. This can be explained by the fact that at a higher pyrolysis temperature less polycyclic naphthenes are formed, alkyl substituents are removed in the formed aromatic compounds and that leads to an increase in the aromatic ring particles in the molecule [7].

The pyrolysis condensate obtained at the optimum temperature of 520–540°C was divided into fractions and their physicochemical properties were investigated. In the analysis of the fractional composition, the yield of the gasoline fraction was 26–28 wt.%. The diesel fraction content was 18–23 wt.% and the residue was 45–47 wt.%. It should be noted that the total output of light products is quite high and is no less than that of light petroleum products. However, the distribution of light fractions is shifted towards gasoline based on diesel, which is not typical of oil.

When comparing the properties of the pyrolysis condensate fractions with the traditional petroleum products (Table 3), one can see that the properties of the fractions obtained are different from those of the traditional refinery fuels.

In particular, the content of sulfur in gasoline and diesel fractions is significantly inflated due to the presence of sulfur vulcanizing agent in the rubber. It is therefore advisable for these fractions to be hydraulically purified before being used as components of the fuel or as feedstock of the relevant processes. The high content of unsaturated hydrocarbons indicates the low stability of the fuel and the need for its rapid use. However, this shortcoming can be overcome by shortening the fuel storage life by prioritizing its use in fuel mixtures.

Comparative analysis of physicochemical properties of pyrolysis condensate and oils

Table 1

Oil	Density at 20°C, kg/m ³	Molecular weight, kg/kmol	Kinematic viscosity at 20°C, mm ² /s	Mass sulfur content, %
Dolynska	847.6	206	—	0.20
Bytkovska	878.0	218	—	0.50
Orovska	858.0	209	—	0.55
Ulychnyanska	827.0	201	10.08	0.38
Lelyakivska	804.5	170	3.21	0.70
Gnidyntsivska	830.7	190	4.02	0.47
Kachanivska	843.0	209	13.90	0.70
Hlynko-Rozbyshivska	840.0	220	8.10	0.70
Prylukska	825.4	219	22.1	0.41
Rybalska	842.7	216	7.59	0.30
Novohryhorivska	814.3	248	4.92	0.10
Pyrolysis condensate	898.0	205	4.59	0.4–0.5

Table 2
Structural-group composition of the pyrolysis product*

Pyrolysis temperature, °C	Ct	Car	Cn	Cp	Rt	Rar	Rn
350	95.2857	16.6142	78.6715	4.7143	1.8183	0.2560	1.5623
400	77.7726	21.4635	56.3091	22.2274	1.7191	0.4020	1.3171
500	54.3235	39.1511	15.1724	45.6765	1.2658	0.8604	0.4054
600	48.9415	48.3600	0.5815	51.0585	1.0664	1.0486	0.0178

Note: * – Ct is the carbon content in the ring (aromatic and naphthenic) structures, wt.%; Car is the carbon content in aromatic structures, wt.%; Cn is the carbon content in naphthenic structures, wt.%; Cp is the carbon content in paraffin structures, wt.%; Rt is the total number of rings in the molecule (aromatic and naphthenic); Rar is the average number of aromatic rings in the molecule; and Rn is the average number of naphthenic rings in the molecule.

Table 3
Comparative analysis of experimental fractions with traditional fuels

Indicator	Fraction 85–180°C from pyrocondensate	Gasoline fraction 85–180°C from oil	Fraction 180–350°C from pyrocondensate	Diesel fuel	Fraction 350°C – end of boiling from pyrocondensate	Fuel oil (the state standard GOST 10585-2013)
Density at temperatures 20°C, kg/m ³	769	770	885	800–845	972	not standardized
Sulfur content, wt.%	1.07	0.061	1.42	0.035	2.25	0.5–3.5
Viscosity at the temperature of 20°C, mm ² /s	0.77	0.68	1.79	1.5–4.0	132.65	–
Mass fraction of aromatic hydrocarbons, not more than, %	41	17.5	51.09	11.0	–	–
Mass fraction of unsaturated hydrocarbons, %	13.14	18.0	–	–	18.67	–
Molecular weight, g/mol	87.56	–	135.7	172.3	235.57	–
Ash content, %	–	–	0.55	0.01	0.0079	0.05
Appearance	transparent and light, without mechanical impurities and water	transparent and light	brown liquid	light brown liquid	dark, viscous liquid	dark, viscous liquid

The content of aromatic compounds, densities and viscosity are slightly increased, but these fractions can be used by adjusting the required fuel composition.

Regarding the properties of the fraction 350°C (the end of boiling), this residue of pyrocondensate meets the standard requirements for fuel oil. This allows involving this fraction as a component of boiler fuels.

Conclusions

Pyrolysis of solid polymer waste (car tires) in the temperature range of 520–540°C provides complete decomposition with a yield of liquid product of up to 58%. The resulting pyrocondensate contains up to 55% light products. An increase in the pyrolysis temperature leads to a decrease in the proportion of polycyclic naphthenes and an increase in the proportion of the aromatic ring in the molecule due

to the cleavage of alkyl substituents.

The obtained hydrocarbon fractions in the processing of spent tires are similar in properties to traditional petroleum fractions, but a further use of the obtained products is possible only with the refinement of known methods used for petroleum fractions.

The results of the study showed the feasibility of using this method of recycling worn car tires, which can simultaneously address two pressing issues: the disposal of waste hazardous to the environment and obtaining a promising product as an additional source of replenishment of raw materials for fuel.

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ПІРОЛІЗ ТВЕРДИХ ПОЛІМЕРНИХ ВІДХОДІВ ТА ВЛАСТИВОСТІ ОДЕРЖАНИХ ПРОДУКТІВ

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Досліджено піроліз твердих полімерних відходів (автомобільних шин) в інтервалі температур 350–650°C протягом 15–105 хв. Встановлено, що максимальний вихід рідкого продукту (58%) спостерігається в інтервалі температур 520–540°C. Виконано порівняння одержаного піроконденсату з нафтою і показано, що піролізний конденсат досить важкий, але має низьку кінематичну в'язкість та помірну молекулярну масу. Встановлено, що при піролізі гуми більша частина сірки залишається у твердому залишку від 1,27 до 2,1 мас.%. Присутність 12,9% ненасичених вуглеводнів у піролізний олії обумовлюється наявністю подвійних зв'язків у каучуках та утворенням подвійних зв'язків при деструкції полімерів. Встановлено, що збільшення температури піролізу з 400 до 600°C приводить до зменшення поліциклічних наftenів та збільшення частки ароматичного кільця у молекулі за рахунок відщеплення алкільних замісників. Показано фракційний склад продуктів піролізу, одержаного в інтервалі температур 520–540°C. Вихід бензинової фракції склав 26–28 мас.%, дизельної фракції – 18–23 мас.%, залишку – 45–47 мас.%. Порівняння властивостей одержаних фракцій з піроконденсату з традиційними нафтопродуктами показало, що вміст сірчаних сполук для бензинової та дизельної фракцій завищений через наявність в гумі вулканізуючого агенту сірки. Вміст ароматичних сполук, показники густин та в'язкості є дещо підвищеними в цих фракціях. Властивості фракції 350°C (кінець кипіння) майже не відрізняються від топкового мазуту.

Ключові слова: автомобільні шини, піроліз, паливо, небезпечні речовини, екологічна проблема, піроконденсат, утилізація.

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Keywords: car tire; pyrolysis; fuel; dangerous substance; environmental problem; pyrocondensate; utilization.

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