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ESTIMATION OF POSSIBILITY OF TYRE UTILIZATION PRODUCTS USAGE AS ALTERNATIVE FUEL

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Abstract. *It was shown that without additional processing neither solid nor liquid products of tire pyrolysis can be used in practice. The purification methods of pyrolysis liquid used for installations are proposed. They offer to use liquid products as alternative diesel fuel, solid products - as alternative fuel for energy installations.*

Key words: *worn tyre recycling, slag, alternative fuel, pyrolysis.*

ОЦЕНКА ВОЗМОЖНОСТИ ИСПОЛЬЗОВАНИЯ ПРОДУКТОВ УТИЛИЗАЦИИ ШИН В КАЧЕСТВЕ АЛЬТЕРНАТИВНОГО ТОПЛИВА

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Аннотация. *Обоснована невозможность использования на практике без дополнительной обработки жидких и твердых продуктов пиролиза шин. Предложены способы очистки пиролизной жидкости. В качестве альтернативного дизельного топлива предложено использовать пиролизную жидкость, а твердые продукты – для энергетических установок.*

Ключевые слова: *утилизация шин, пиролизный шлак, альтернативное дизельное топливо.*

ОЦІНКА МОЖЛИВОСТІ ВИКОРИСТАННЯ ПРОДУКТІВ УТИЛІЗАЦІЇ ШИН ЯК АЛЬТЕРНАТИВНОГО ПАЛИВА

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Анотація. *Обґрунтовано неможливість використання на практиці без додаткової обробки рідких і твердих продуктів піролізу шин. Запропоновано способи очищення піролізної рідини. Як альтернативне дизельне паливо запропоновано використовувати піролізну рідину, а тверді продукти – для енергетичних установок.*

Ключові слова: *утилізація шин, піролізний шлак, альтернативне дизельне паливо.*

Introduction

Global stocks of worn vehicle tires rate ranges from 25 to 39 million tons with an annual growth not less than seven million tons.. Places of tire clusters present a favorable habitat for breeding of a number of rodents and insects, which are carriers of various diseases. Moreover, the tires have a high fire risk, and the products produced during uncontrolled burning adversely effects the environment (soil, water, air pool).

The extent of tire utilization is from 95 to 100 % in developed countries. According to the European Association of Tire Recycling (EATR), the

volume of shock-resistant tires has increased fivefold from 1994 to 2010. [1]. Every year, in Ukraine there is produced 200 000 tons of waste tires, but no more than 10 percent of tires is utilized. In our opinion, the technique of pyrolysis can become one of the most attractive ways of tire utilization in Ukraine, as a result of waste reclamation there are produced substances that can be used as fuel.

Analysis of literature

The most widespread techniques of tyre recycling in Europe are thermal processing and mechanical crushing, the utilization rate of which is 30 – 50 % of the total mass of utilized tyres [1]. One of the most common thermal methods of rubber waste utilization is pyrolysis. As a result, there always evolve three products: gas (about 12 %), liquid (about 35 – 52 %) and solid carbon product (slag) (about 36 %).

The opinions of scientists on the utilization of pyrolysis products are controversial. It is believed that the most valuable product is the pyrolysis liquid that can be used as a raw material for producing motor fuels and valuable hydrocarbons. There are known examples of pyrolysis liquid utilization as fuel for boiler installations [2]. The mixture of waste oil and pyrolysis liquid is proposed to be used as fuel in boiler units [6]. Another point of view is held by scientists who point out significant differences in pyrolysis liquid properties and traditional fuels, which do not allow using it as a substitute fuel [3–5].

It is considered that the solid product-slag can be used as adsorbents and fillers in the manufacture of rubber.. It can't be used as a substitute of carbon in rubber mixtures without appropriate treatment. This is due to the fact that its basic characteristics are 2–2,5 times worse than of the activated carbon standard samples [6]. The pyrolysis slag obtained from worn tyres has a certain sorption capacity, indicating the possibility of using it as a sorbent, but only after additional activation [5, 6]. For example, the ash content in the pyrolysis slag is 7, 7–16 % and for standard samples of carbon – 0,45 %. The specific geometric surface of slag is 39–43 m^2/g, and in standard carbon samples is 50–100 m^2/g. According to our data and the data [7] represented by manufactures of the pyrolysis plant «Alfa», the sorption capacity of slag is significantly lower than that of the activated carbon used as the adsorbent.

In 2002, a special commission of the European Union «CRAFT» in 2002 developed a project «Recycle Tyre Contract GIST-CT-2002» to find out practical ways of cleaning the products of tyres pyrolysis. Under this project, at the C Bp Carbon plant in Hungary they produced an ecologically clean fuel with a low content of carbon and air pollutants. Employment of such technology, as stated in the report of the commission, will ensure the usage of pyrolysis slag in the given industry. Carbon Industries is planing to open new factories in Europe, North America and Australia [8]. Thus, in the process of rubber waste utilization by pyrolysis method they obtain solid slag. Without additional processing that requires special equipment and reagents it can't be applied in practice [6]. Thus, the method of tire recycling by pyrolysis has its advantages and disadvantages. The advantages of the given method include: low power consumption; the possibility of recycling different type of tires as well as conservation of fossil fuels. The disadvantages of the given method are: low-quality of products that greatly limit its practical use and a specific, unpleasant smell characteristic of liquid pyrolysis products. This is the main bar to tire pyrolysis technology spreading.

The purpose and tasks of the work

The given research deals with the method of pyrolysis. It's a well-known fact that the problem of energy independence is a high-priority one in the energy policy of Ukraine and many other countries. The authors' attempt lies in developing an alternative fuel, using worn tires. In our opinion, the relevance of tire recycling and obtaining an alternative fuel is the following:
– recycling of tires will help protect the environment from the harmful effect produced by tire landfills;
– raw material (oil) can be saved and partly replaced by tire pyrolysis liquid;
– production of alternative fuel based on worn tire utilization will provide jobs for a large number of people employed at pyrolysis plants and contribute to the development of small business in Ukraine.

The purpose: to define the methods of improving the quality of pyrolysis liquid and slag to be used as alternative fuel. To achieve this goal it was necessary to solve the following tasks:
– to define the methods of purification of tire pyrolysis products from harmful compounds;

– to find the optimal method of pyrolysis liquid purification;
– to assess the possibility of using liquid pyrolysis products for production of the alternative diesel fuel.
– to define the method of using solid products of tire pyrolysis as an alternate of coal for stationary power plants.

Investigation of tire pyrolysis product properties

In recent years, in the countries of the European Union, as well as Russia, Ukraine there have been obtained many patents on recycling of tires by pyrolysis [3, 6, 7]. Developers of these systems claim that all three tire pyrolysis products, such as gas, liquid and solid carbon (slag) can be directly used in the industry. As a proof, they evidence some characteristics of pyrolysis liquid and slag, which are similar to conventional fuels. However, we are not aware of any significant facts that would indicate that the pyrolysis liquid or slag has been ever used in the industry for a long time with a positive result without being worked up. In our opinion, the pyrolysis of worn out tires can become one of the most attractive ways of tire utilization in Ukraine, as it could enable to obtain raw material to be used for production of fuel that is so important for our country. Studies on properties of the tire pyrolysis liquid have been conducted at the Department of Environmental Protection for several years. In investigations there were used solid and liquid recycling products of tires which were obtained, using Ukrainian pyrolysis installations. It has been proved that without extra treatment of liquid products, pyrolysis can't be used in the industry. There have been many proposals on pyrolysis installations in Ukraine recently. The characteristics of pyrolysis products varied at different installations. Installation manufacturers state that all three products are commercial goods and therefore the installations are profitable. Our analysis of economic indexes of installations showed that actually the products in question are not sold and the enterprises aren't profitable and do not pay off quickly [9, 10].

We decided to explore the possibility of modifying the properties of tire pyrolysis products in order to use them in practice as substitutes for traditional fuels. First of all we decided to define the main physical and chemical properties of pyrolysed liquid products and to compare them with the corresponding properties of traditional fuels. The results of our research are presented in [11]. In our research we used standard methods of liquid fuel analysis. In article [11] we identified the main differences in the properties of pyrolysis liquid and traditional fuels.

The difference between the properties of pyrolysis liquid and of typical fuels is identified by the values of cinematic viscosity, ash and sulphur contents. Furthermore, the water content substantially exceeds the standard. The pyrolysis liquid has a specific harsh and unpleasant smell. The content of aroma compounds in pyrolysis liquid is 93 %. These compounds are easily oxidized, polymerized, producing resinous fallout. The developers of «Shakh» company offer to use their installations for pyrolysis liquid fractionation. Russian manufacturers of modern pyrolysis installations claim that their plants produce 3 types of fuel: gasoline, diesel and fuel oil [11]. The pyrolysis fuel, according to the developers of «Shakh» company, is an analogue of fuel oil M100. We cut the pyrolysis liquid into fractions. The results can be seen in paper [10].

However, after fractionation there remain harmful substances. According to our results, we have concluded that without additional purification the pyrolysis liquid can't be used as fuel. We have determined that only two methods used for purification of oil products from harmful substances can be used for the pyrolysed liquid. They are sulphur acid purification and hydropurification. Only these two methods make it possible to simultaneously remove mercaptans and unsaturated aromatic hydrocarbons from petroleum. Hydropurification turns out to be the most environmentally-friendly method. At the next stage, there was conducted research with the purpose of reducing both the unpleasant smell and the pyrolysis liquid corrosion activity. In further research it was decided to determine the optimal conditions for pyrolysed liquid hydropurification. The hydropurification efficiency was checked by the iodine number.

The results of the experiment provide the principal possibility of using this method for the pyrolysed liquid but require more efficient conditions. At the Department of Ecology of KhNAHU there were identified specific conditions for pyrolysis liquid hydropurification. According to the research results we obtained a patent «Alternative Diesel Fuel» [12].

The lack of this technology lies in the possibility of applying it only at high-power installations and enterprises. In Ukraine there are mainly used small pyrolysis plants which are designed to produce 1-3 tons of the pyrolysis liquid per day. So it was decided to make an attempt to improve the properties of the pyrolysis liquid with the help of chemicals in such a way that it could be directly used at small plants without using special equipment. Modified pyrolysis liquid can be used as an alternative to diesel fuel. The experiments have shown that the conditions for modification of diesel oil fractions are not suitable for pyrolysis liquid deodorization in the industry at present. Therefore, in this study there were determined the conditions of pyrolysis liquid processing by specific reagents, which makes it possible to reduce the intencity of a specific smell as well as the concentration of sulfur compounds. The concentration of sulfur compounds before and after the treatment of the pyrolysis liquid by chemical reagents has been determined according to the standard method, the method of potentiometric titration. It has been proven experimentally that after the treatment of the pyrolysis liquid with a certain reagents, the concentration of sulfur compounds decreases and this makes it possible to apply the pyrolysis liquid for producing an alternative diesel fuel. We have developed an alternative diesel fuel composition. It consists of a mixture of traditional diesel fuel and the purified liquid obtained by pyrolysis of utilized tires. According to this research yielded a second patent «Alternative diesel fuel» [13].

At the next stage of our work we investigated the possibilities of using the pyrolysis slag as fuel for industrial energy plants. The necessity to reduce the total cost of fuel by partially replacing it by wastes is a major incentive for seeking cheap alternative fuels for energy plants. To use the slag as a fuel, it was necessary to show that the environmental marks of the slag were not at least worse than those of the coal. With this purpose, we investigated the chemical composition of ash and gases, which are formed during slag combustion, as well as carried out technical analysis of slag according to standard procedures. Comparative analysis of the properties of pyrolysis slag and Donetsk coal of grade ASH are shown in Table 1. The properties of slag are based on the results of our own measurements [6] as well as the data presented in studies [14].

The results of technical analysis of slag that characterize its practical value for the purpose of burning are shown in Table 1.

Table1 Results of technical analysis of slag and coal of grade ASH

GOST	Indicators	Donetsk coal of grade ASH	Data for slag for Ukrainian pyrolisisplants, %
11014-81	Humidty, %	0,4–1,5	0,32–2,9
11022-95	Ash content, %	2–29	7,7–16,8
6382-2001	Volotile output, %	to 8 %	1,8–5
2408.1-95	Carbon (C)	90–98	88–94,0
9318-91	Hydrogen (H_2)	1,2–3,6	1,89–4,8
9318-91	Nitrogen (N_2)	0,7–1,6	
9318-91	Oxygen (O_2)	0,6–2,5	
2059-95	Sulfur (S)	0,7–3,7	1,1–3,6
147-95	Energy value (Q(MJ/kg)	21–24	23,5–31,9

As shown in Table 1, the ash content in the slag is less than in the coal of grade ASH, so partial replacement of coal by slag results in particulate emissions reduction. There is no increase of sulfur emissions, and calorific fuel capacity (Q) is not reduced, and in some cases is even increased. We offer to use as a fuel the mixture of slag and coal, using pyrolysis slag as a partial substitute of conventional fuels for power plants. According to this research, we obtained two patents for the method of using solid products obtained by recycling utilized tires by pyrolysis method as an alternative fuel for power plants [15, 16]. The research conducted makes it possible to draw the following conclusions.

Conclusion

The ecological estimation of tire utilization has been conducted by the method of pyrolysis. It has been shown that without further processing solid and liquid products of tire pyrolysis can't be used in practice.

Analysis of modern industrial methods of demercaptanization and deodorization of oil products have been conducted. It has been shown that simultaneous removal of organic

sulfur and unsaturated carbon compounds is possible only by means of hydropurification; It has been proven that the application of pyrolysis liquid hydropurification at low-power installations is inefficient.

The fundamental possibility of deodorization of the pyrolysis liquid that was obtained as a result of worn tire utilization by chemical reagents is experimentally shown. Optimal methods for deodorization of pyrolysis liquid diesel fractions at low-power installations are specified.

The ways to improve the quality of liquid products obtained by pyrolysis of worn out tires that gives an opportunity to use them as an alternative diesel fuel is proposed.

A mixture of pyrolisis slag and coal after special processing is proposed to be used as a substitute of coal in boiler plants.

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