Vol. 2, No. 4, 2017

THE WORN TYRES PYROLISIS' SOLID PRODUCTS OPPORTUNITY APPLICATION AS FUEL SUBSTITUTE ASSESSMENT

Olena Pozdnyakova, Nataliia Vnykova

Kharkov National Automobile and Highway University,
25, Yaroslava Mudrogo Str., Kharkov, 61002, Ukraine,
pei.xadi@gmail.com, ecologyknady@gmail.com

Received: 15.11.2017

Abstract. It has been shown that, without additional processing pyrolysis products of tyres cannot be used in practice. The mixture of pellets-pyrolysis char-coal have been proposed as an alternative fuel for energy plants.

Key words: end of life tyres, char, pyrolys

Introduction

One of the most common methods of utilization of rubber waste is pyrolysis. As a result, it always comes out three products: gas (about 12 %), liquid (about 35–52 %) and solid carbon product – char (about 36 %). The relation between the products of pyrolysis depends on many factors. The opinions of scientists on the utilization of pyrolysis products are controversial. It is believed that the most valuable products is the pyrolysis oil that may be usable as a raw material for motor fuels and valuable hydrocarbons [1]. There are known examples of the utilization of pyrolysis oil as fuel for boiler installations [2]. The mixture of waste oil and pyrolysis oil is proposed to be used as fuel in boiler units [3]. The solid product-char can be used as adsorbents and fillers in the manufacture of rubber and other mixtures.

Another point of view is held by scientists, who point out essential differences in properties of pyrolysis oil, pyrolysis char and ordinary fuels, which does not allow using it as a succedaneum fuel [4, 5, 6]. Pyrolysis char is essentially low quality [3]. It can't be used as a substitute of carbon in rubber mixtures without appropriate treatment. According to ETRMA [4] report, the econ**o**mic viability of pyrolysis is hampered by the fact, that the prices obtained for the by-pr**o**ducts, often fail to justify the pr**o**cess costs.

Thus, the method of tyre recycling by pyrolysis has its advantages and disadvantages. The advantages of the method include: low power consumption; the ability of any tyres recycling and the nature reserve of fossil fuels. The disadvantages of the method are: low-quality products that greatly limit its practical use and specific, unpleasant smell, which liquid pyrolysis products have.

Recently, the relation to the process of pyrolysis of worn tyres is changing. The development of modern technologies contributes to the improvement of pyrolysis products quality. Therefore, a number of companies in the world are developing and exploiting new technologies of worn tyres pyrolysis. The tyre recycling industry in the USA is among the strongest and most spread worldwide. According to the U.S. Environmental Protection Agency (EPA) pyrolysis of scrap tyres offers an environmentally attractive and cost-effective method for transforming of the waste tyres into useful products, heat and electrical energy [7].

Significant successes in this way were achieved by American firms Pyrolyx USA which plans to build the largest plant in the world and Delta-Energy Group whose DEPolymerization process produces two different lines, Phoenix Black and Zephyr Black. [8]

In addition, the technology of worn tyres pyrolysis is actively developing in Poland, where new types of pyrolysis reactors are proposed. [2].

Chinese manufacturers affirm that they produce diesel fuel from liquid pyrolysis products with no unpleasant odor. The fuel for boiler installations generated at Chinese manufactures meets the European standards. According to [9] this firms sell their equipment to 34 countries of the world.

In view of the above, we decided to test the possibility of using pyrolysis char in the Ukrainian industry.

The actuality of the research

Urgent research is devoted to the method of pyrolysis. In our opinion, the pyrolysis of tyres carried out using modern technologies can provide the Ukrainian industry with valuable alternative fuel. We

want to develop an alternative fuel from end of life tyres (ELT). In our opinion, the benefits of tyre recycling and creation alternative fuel are:

– recycling of tyres will help to protect the environment from tyres landfills;

– raw material (coil and oil) can be saved and partly replaced with products from the pyrolysis of tyres;

– we offer to produce alternative fuel from waste without use of food raw materials.

The purpose and the tasks

The purpose of the research is to define the factors that provide the application of solid pyrolysis products received from the ELT as alternative fuel. To achieve this purpose it was necessary to decide the following tasks:

– estimate the environmental performance of pyrolysis char;

– to evince that using of the char will not reduce the calorific value of fuel;

– present that the use of the char will not increase the emission of toxic substances;

– to find a way how to use the tyre pyrolysis char for partial replacement of coal in power plants;

We set the task to develop an alt**e**rnative fuel from worn tyres. The properties of tyre pyrolysis products were analyzed.

The results of the experiments and their discussion

In the United States the standardization of recycled carbon black (pyrolysis char) is soon going to be implemented in industry. American Society for Testing and Materials (ASTM) has introduced opening of the committee which will develop standards for the pyrolysis char in 2017. The goal of the ASTM's new committee (D36) will be to establish and update standards in ELT and scrap rubber decomposition, standards in material characteristics and sustainability [10].

According to EuroEco Fuels [11] they are building a state of the art facility and their conversion technology produces petrochemicals and fuels from wastes, for example carbon filler and coal for energy generation.

At the Department of Ecology of Kharkiv State Automobile Highway University in Ukraine, we decided to evaluate the possibility of using the tyre pyrolysis products in the industry of Ukraine.

We analyzed the compliance with the standard requirements for absorbents of pyrolysis char and samples of typical П234 and П803 adsorbents [3]. The results are presented in Table 1.

Table 1

Comparative analysis of the properties of worn-out tyres pyrolysis char and standard carbon black samples

Property description	П 234	Char	П 803
Specific geometric surface, m^2/g	95–100	39–43	50
Dibutyl phthalate sorption capacity, $cm^3/100g$	101 ± 4	60 ± 7	83 ± 7
Iodine number, g / kg	105 ± 6	45 ± 5	–
Mass fraction of total sulfur, %	1.81	1.1–2.1	1.1
Ash content, %	0.45	7.7–16.8	0.45
pH aqueous extract	10.25	7–10	7–9
Bulk density, kg / m^3	340	430	300–400

According to the results our research, the pyrolysis char cannot be used as a substitute of carbon in rubber mixtures without appropriate treatment. Thus, the basic characteristics of pyrolysis char are than 2–2.5 times less than carbon standard samples. The char has a sorption capacity, indicating the possibility of using it as a sorbent, but only after additional activation [1, 3]. For example, the ash content in the pyrolysis char is 7.7–16 % and for standard samples – 0.45 %. The specific geometric surface is 39–43 m^2/g, and in standard samples of 50–100 m^2/g. The sorption capacity of char is significantly lower than that of activated carbon used as the adsorbent according to our knowledge and to the dates of [12].

In the next stage of our work, we investigated the possibilities of using the pyrolyses char as fuel for industrial energy plants. The necessity to reduce the total cost of fuel by its partial replacement from wastes is a major incentive to find cheap alternative fuel for energy plants. To use the char as a fuel it was necessary to show that the environmental marks of the char, at least, are not worse than those of coal. For this purpose, we investigated the chemical composition of the ash and gases, which are formed during char combustion. The results of the technical analysis of char that characterize

its practical value for the purpose of burning are shown in Table 2. As shown in Table 2, the ash content in the char is less than coal of anthracite, so the partial replacement of coal char reduces emissions of toxic components.

According to the data from Table 2 the emission of sulfur does not increase and heat of combustion (Q) is not reduced, and in some cases even increased. The water content of the char does not exceed its content in coal. The moisture content of char does not exceed its content in coal. The content of the main combustible components - carbon and hydrogen in char practically does not differ from coal. According to these results, we came to the conclusion that char can be used as a substitute for coal.

Table 2

Results of technical analysis char and coal anthracite

Standards numbers	Indicators	Coal anthracite	Ukraine char, %
11014-81	Humidity, %	0.4–1.5	0.32–2.9
11022-95	Ash, %	2–29	7.7–16.8
6382-2001	Water content, %	0.4–1.5	1.8–5
2408.1-95	Carbon, %	90–98	88–94.0
9318-91	Hydrogen, %	1.2–3.6	1.89–4.8
9318-91	Nitrogen, %	0.7–1.6	
9318-91	Oxygen, %	0.6–2.5	
2059-95	Sulfur, %	0.7–3.7	1.1–2.1
147-95	Q, MJ/kg	21–31	23.5–31.9

Recently thermal power stations are co-incinerating coal increasingly with wood pellets in Europe and North America. Especially widely such fuel mixtures are used in USA, Great Britain, Netherland, Poland and Spain. The main advantage of co-incineration is the possibility to use existing coal combustion equipment. It provides the lowest capital costs compared with the construction of new boiler units. Such technology allows to utilize a significant amount of biomass, partially replace fossil fuels and reducing emissions of nitrogen oxides and sulfur oxides [13]. Among the varieties of technology for co-incineration of coal and biomass, flaring combustion systems was the most widespread. The distribution of this technology was obtained in the United States, Great Britain and Finland. There are two main principles of using industrial pellets for energy production: burning only pellets as fuel or burning the mixture of pellets and coal.

Last years the Institute of Coal Energy Technologies of the National Academy of Sciences of Ukraine conducts research of co-incineration biomass and Ukrainian coal. Most of the Ukrainian power plants operate using flaring combustion systems [14]. The use of biomass for combustion with coal is especially relevant for this technology. At the same time not only the environmental performance of the power plant is improved, but it also the cost of fuel and heat energy is being reduced. For example, the replacement of only 5 % of coal by pellets at a 2000 MW power plant provides utilization of 375,000 tones of biomass per year [15]. However, the specific properties of pellets limit their content in mixture as not more than 10–20 %, and confidently – 5–10 % [16]. Various schemes of co-incineration coal and pellets were explored abroad [15]. The technology of co-incineration pellets with coal is considered to be the most promising, at which biomass is prepared in an autonomous feed and grinding systems. Next, the pellets are burned in such systems that are optimized for combustion of biomass.

It was found that the content of pellets in the fuel mixture should not exceed 40 % otherwise the emission of nitrogen oxides to the atmosphere dramatically increases. In [17], it was shown that with content of pellets in the mixture of more than 40 %, fractional bundle is observed. According to other data [18], in Denmark industrial equipment burns a mixture of 50 % pellets and coal. As biofuel it is possible to use not only granules of wood waste, but also granules of sunflower [19]. As can be seen, there is no consensus on the allowable content of pellets in fuel mixtures with coal. Thus, there are next results of co-incineration of pellets and coal at the power stations:

– reduction in the cost of fuel for power plants (for example in the United States the cost of pellets is almost 20 % lower than the cost of coal);

– reduction of emissions of sulfur and nitrogen oxides, as well as of ashes;

– reduction of biomass discharge into the dumps;

– reduction of greenhouse gas emissions due to the decomposition of biomass in dumps;

– saving of natural resources as coal;

– use of local biofuels.

The current issue for Ukraine is the replacement of natural gas by coal. Indeed, an essential economic effect with such kind of replacement will be received when using cheap fuel. Low-reaction (anthracite and brown coal), or low-quality (high-ash and fine fractional) coal can be used in Ukraine as actually interesting. Deposits of such coal are located in various regions of Ukraine.

In modern economic conditions, Ukraine does not have an opportunity to equip small and medium power plants with cost effective and environmentally sound manner equipment. Coal which is used in Ukraine has high ash content, which can reach 40 %. This results in significant emissions of solid particles and sulfur oxides. Pellets have very low ash and sulfur content. So the use of such mixtures will reduce emissions of solid particles and sulfur oxides into the atmosphere using the existing in Ukraine equipment even with highly ash coal. However, pellets have significantly lower heat of combustion than coal. Taking into account the properties of pellets and pyrolysis char of ELT, we decided to propose to apply them in a coal-pellets-ELT char triple mixture.

At the KhNADU Department of Ecology the research of the coal-pyrolysis char of ELT mixtures properties was carried out. It was decided to estimate the environmental performance of the triple mixture of coal-pellets-char. The use of the pellets in such mixture will reduce the emissions of solid particles and sulfur dioxide. Char addition will allow increasing the heating value of the fuel mixture.

As can be seen in Table 2 the ash content in the pyrolysis char is less than in the coal anthracite. Therefore, when the coal is replaced with char the emissions of solid particles decreases. In this case there is no increase in emissions of sulfur, the heating value of fuel does not decrease and even increases in some cases. It was necessary to identify such compositions, which would allow disposing waste of worn tyres and reducing the use of coal.

In order to increase the fuel briquettes' heat of combustion and reduce ash emissions we proposed to use pyrolysis char instead of coal.

The task of our research was: to ensure the utilization of solid pyrolysis products; to use of wood waste (pellets) with simultaneously saving traditional solid fuel; to reduce the emission of toxic substances from power plants.

At first, we analyzed the environmental properties of pellets. The analysis was carried out on the contents of ash and sulfur pellets. Calorific value of pellets was also analyzed. In 2010, EU countries developed uniform standards for wood pellets quality, called the “Enplus”. The initiators of its development and implementation were the “The European Biomass Association” and the “European Pellet Council” non-profit organizations. The owner of the “Enplus” trademark is the “European Biomass Association” [20].

To date, this type of certificate is mandatory for wood pellets manufacturers. Comparative characteristics of wood pellets according to Enplus are presented in Table 3.

Table 3

ENplus standards for wood pellets quality

Characteristics	Units of measurement	ENplus-A1	ENplus-A2	ENplus B
Bulk density,	kg / m^3	≥ 600	≥ 600	≥ 600
Heat of combustion (Q)	Mdj/kg	≥ 16.5	≥ 16.5	≥ 16.0
Water content	%	≤ 10	≤ 10	≤ 10
Ash	%	≤ 0.7	≤ 1.0	≤ 3.0
Sulfur	mg/kg	≤ 0.05	≤ 0.05	≤ 0.05

As can be seen from the table 3, the content of ash and sulfur in pellets is much lower than that of char and coal, but the water content is higher, and Q is significantly lower than in coal and in char. Thus, the replacement of coal with pellets will reduce the efficiency of combustion however it will improve the environmental performance of the process.

In Ukraine there are no uniform pellets quality standards. Therefore, we analyzed the properties of pellets that are produced at existing Ukrainian enterprises (Table 4). According to the Ukrainian Pellet Union, today there are 347 companies registered in the country for the production or sale of solid biofuels. In 2014, they produced 380 thousand tons of wood pellets and 178 thousand tons of wood briquettes. Average capacity of enterprises is 380 tons per month. Although there are factories with a capacity of 5 or even 10 thousand tons per year [21]. The pellets properties of Ukrainian manufacturers are presented in Table 4.

Table 4

The properties of Ukraine pellets

Name of Company	Characteristics of pellets			
	Ash, %	Sulfur, %	Water content, %	Heat of combustion Q, MJ / kg
Bioenergosbyt	1.31	0.02	6.8	18.12–21.20
KievPellets	0.31	0.012	–	18.4
Brig	1.21	–	3.1	20.33
PelletEnergo	≤1.5	–	10	17.7
Promin	0.26	–	8.1	17.93–21.13
Centrum	1	–	7	19
EcobioProm	0.48	0.012	7.8	19.28
EcoGran	0.8	0.01	5.9	18–21
EcoPellet	0.41	0.01	6.73	21
EcoPrime	0.64	0.01	4.5	17.87–20.19
“Barlinek”	0.7	–	10	18.0
“BKM-Wood”	0.9	–	7.05	18.0
“Ditek Pellets”	0.8–1.2	–	7	18.06
“Eco Pellet”	0.65	–	4.37	19.0
“VNT-Group”	0.34	0.01	4.96	19–21

According to the data of Table 4 it is evident that the lowest ash content of pellets is 0.26 % a, the largest – 1.5 %. The minimum sulfur content is 0.01 % and the maximum is 0.2. The maximum heat of combustion is 21.13 MJ/kg, and the minimum is 17.7 MJ/kg. Thus, in any Ukrainian pellets ash content and sulfur content are much less than that of coal and pyrolysis char. The calorific value of pellets can be 30 % lower than char and high-quality coal.

We offer to apply as a fuel a coal-pellets-ELT char triple mixture. We propose to mix pellets with char and coal directly on the power plant. Pre-mixed components may be milled to particles of the necessary size directly on ordinary mills which are equipped with power plants for coal grinding. The char is pre-freed from the metal cord by means of magnetic separation using conventional devices. Two methods are acceptable: a) from the beginning to mix pellets, char and coal in certain ratios, and then add them to the power plant; b) separately add components to the power plant using special devices. We have established the optimum mixing ratio [22]. The inclusion of char in the mixture compensates the reduction of the coal heat combustion by replacing its particles with pellets. It is known that the pellets have significantly less heat combustion.

We recommend using our mixtures as a fuel in such standard power plants, which are suitable for co-incineration of biomass and coal. The using of our alternative fuel allows the next:

– saving energy coal, which is currently lacking in Ukraine;

– use new technologies for application the pyrolysis char from worn out tyres in Ukraine;

– increasing of pellets heat value due to higher pyrolysis char heat of combustion;

– at co-burning with coal, not only biomass wastes, but also worn out tyres wastes will be utilize.

Our fuel mixture can be used in power stations, boiler houses and utility companies where, along with traditional solid fuel (coal), it is possible to use a mixture of pellets and char in certain ratios. We offer wood pellets in certain proportions to mix with pre-shredded char and coal. Such fuel mixtures can be used on stationary power plants of low and average power. The advantage of this method is that the addition of char to the pellet increases the heat value of the fuel mixture and reduces the amount of coal in fuel mixtures.

Conclusions

The analysis of current ELT pyrolysis' products usage in industry has revealed the growing interest to this method in different countries. It was shown that solid pyrolysis products of ELT are mainly applied as adsorbents and traditional fuel substitutes.

The properties of pyrolysis char of TLT that influence the emission of toxic substances are determined. It has been shown that sulfur content in char does not exceed its content in coal, and ash content in char is even smaller than that in coal. Therefore, in our opinion, partial replacement of coal with char will not increase emissions of toxic substances.

The current experience of pellets and coal co-incinerating has been analyzed. It has been proved that existing equipment at Ukrainian low and average power plants have enough potential for using this type of mixture.

The results of experiment have verified that Ukrainian woodworking pellets mainly correspond European standards and have no considerable differences. Their sulphur content is minor and ash content is significantly less than that in coal. But at the same time, the moisture content is greater than that of coal, and the calorific value is much smaller. To improve the properties of fuel mixtures, a triple blend of pellets, coal, and pyrolysis char was suggested as fuel for power plants.

Our suggestion is to produce alternative fuel from wastes without using food raw materials.

In our opinion, the pyrolysis technology can become one of the most attractive ways of tyres utilization not only in Ukraine but in other countries as well.

In our opinion, the technique of pyrolysis can become one of the most attractive ways of tyres utilization for Ukraine and not only for Ukraine.

References

[1] Grytsenko A., Vnukova N., Pozdniakova Ye. Avtomobilnui Tranaport: 2015, No. 36. – C. 42–48.

[2] Michał Ryms, Katarzyna Januszewicz, Witold M. Lewandowski, Ewa klugmann-Radziemska. Ecol. Chem. Eng. S. 2013; 20 (1): 93–107.

[3] Petrenko T. V., Novichkov O. I., Pozdnyakova O. I. Utilizacia vidpracovanux avtomobilnux chin: Doneck: DonNABA, 2007. – 110 s.

[4] Taverne JP. End of life tyres – A valuable resource with growing potential. ETRma End-of-life Tyres Management Report of 2011. http://www.etrma.org/uploads/Modules/Documentsmanager/brochure-elt-2011-final.pdf.

[5] Tulenev M.A. Tverdue Butovue Otxodu No. 4, 2007, S. 42–48.

[6] Gerix Vtorichni Resursu No. 1, 2006, s. 13-16.

[7] Maura Keller American Recycler News July 2017 https://pyrolassist.com/environment/

[8] Michael Blumenthal. Making Tyre-Derived Materials a Commodity: A Comparison of the ASTM & CEN Standards https://pyrolassist.com/tag/carbon/

[9] Used tyre oil to diesel fuel oil refining plant product introduction – Xinxiang Doing Renewable Energy Equipment Co., Ltd – Website: http://www.china-doing.com

[10] Feature recovered carbon black. ASTM Standardization News March/April 2017 https://www.sustainable-materials-group.com/Downloads/Pdf/ASTM %20rCB % 20article.pdf www.astm.org/sn /

[11]Euroeco Fuels Poland http://www.euroecofuels.com/

[12] http://a-alfa-ua.woodex.ua/.a-alfa-ukraina.uaprom.net›Kiev›Kategoria@Obladnania dlia vurobnitstva biopaluva.

[13] Nazarov S. M., Kalinin E. V., Isemin T. V. http://www.rosteplo.ru/Tech_stat/stat_shablon.php?id=2325

[14] Chydlo T. C., Dynaevskaia N. I., Beschenui I. V., http://docplayer.ru/42497347-Sovmestnoe-szhiganie-uglya-i-biomassy-v-fakelnyh-kotloagregatah.html.

[15] Golubev V. A. Obosnovanie I soverchenctvovanie spocobov energeticheskogo ispolzovania rastitelnux otxodov. Disertaciy na soickanie ychenoi stepeny k. t. n., Barnaul 2014. http://altstu.ru/media/f/Dissertaciya-Golubeva-VA.pdf

[16] F. J. Frandsen, F. J. Nielsen, P. A. Jensen et al. // print conferencii Engineering Foundation: “Impact of mineral impurities in solid fuel combustion”. – Kona, USA, 2–7 noyabrya 1997.

[17] Viriasov D.M. Psevdocgilenye I sjiganie biotopliva v mnogokomponentnux cloyax. Avtoreferat na soickanie ychenoi stepeni k. t. n. Moskva – 2013.

[18] Mayers M,B.(US) Dgey D,(US) [http://www.findpatent.ru/patent/251/2510660.html]Patent USA №61/181101, 26 travnya 2009, Patent USA No. 61/245506.

[19] ISSN 02043602. Promuchlenaya teplotechnika 2006, t. 28, No. 1.

[20] Pydnitskiy S. Ukrain biotoplivny portal. http://pelleta.com.ua/articles-drevesnye-pellety-zakonodatelnye-i-prakticheskie-3.html

[21] Wood pellets Ukrainian production http://aw-therm.com.ua/drevesnye-pellety-ukrainskogo-proizvodstva

[22] Tyrenko A. M. Vnykova N. V. Pozdnyakova O. I. Patent 107263 Ukraine, Publ. 23.05.16, Buleten No. 23/2014.