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GASEOUS PRODUCTS FROM SCRAP TIRES PYROLISIS

GAZOWE PRODUKTY POCHODZĄCE Z PIROLIZY OPON SAMOCHODOWYCH

Abstract: In European Union 75% of used tires should be recycled. The most common method of used tires disposal, is burning in cement kilns, which does not solve the problem. Pyrolysis process can be an alternative way of utilization of tires. The aim of the researches was to check the influence of pyrolysis products (gas and oil fractions) on environment. Samples from pyrolysis process, like light oil fractions or pyrolysis gases were analyzed using gas chromatography. The pyrolysis installation should be hermetical, because of the PAHs which were detected in a light fraction of oil. In exhaust gases BTEX and PAHs were not detected.

Keywords: pyrolysis process, tires, utilization, gas products

The main directives in European Union about management waste tires are: *The Waste Landfill Directive* (1999), which bans the landfilling of tires since 2006 and another *The End of Life Vehicle Directive* (2000) that forces the separate collection of used tires and encourages to recycle them. Pyrolysis of used tires as an incineration process has been taken into consideration in *Waste Incineration Directive* (2000) [1]. This document concerns very restrictive value of emission gases (pollutants). In the European Union exist a lot of directives and acts which are controlling industry and their chemical effects. There are plenty of regulations about environmental protection. One of them is Directive No. 1907/2006. The law entered into force on 1 June 2007. It is about *Registration, Evaluation and Authorization of Chemicals* (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC (EC 1907/2006) and repealing Council Regulation (EEC) No. 793/93 and Commission Regulation (EC) No. 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

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This directive is to improve the protection of the environment and human health. Responsibility for carrying out risk assessment and testing of the substance was transferred from government to industry. Manufacturers and importers have been obliged to register the information about the substances in a central database. Central database is in Helsinki and it is run by the European Chemicals Agency. This directive forces responsibility on industry to manage the chemicals. The REACH regulation required to provide information about the substances and the risk of them. This regulation exists because of the problem with a large number of substances on the European market which are not controlled. It is important to know where and how many substances are produced. This information can help to identify and implement the risk of management of environmental protection. In this article the research of the gaseous pyrolysis products and their influence on the environment, mostly on air, was done.

Management of used car tires is today one of the major environmental problems, which for years has been solved in several ways. Tires are a valuable material due to the physical and chemical raw materials used in their production. Management of waste tires includes the identification, collection and segregation as well as transportation and disposal through recycling. Waste recovery makes it possible to transform one of the main streams of waste-tires into energy or valuable products that can be reused. It is very important that all of the tire components can be reused.

Since 2006 the prohibition of storage of waste tires in any form is in force and this regulations order that management must be done through:

- recycling of product,
- material recycling (mulching, devulcanization)
- recycling of energy,
- pyrolysis,
- retreading.

The main ingredient of tires is rubber. Rubber is produced by cross-linking of polymeric bonds with sulfur. Tires cannot be easily disposed without using extra energy. About 180÷190 thousand Mg (tons) of new tires is produced during the year in one medium country in European Union. On this basis, we can specify the amount of waste arising from the fact the tires wear out while driving. Up to 20% new tires are on the road in the form of dust. As a result every year we get about 150 thousand Mg (tons) of used tires. In past years the number of scrap tires has been increased with increasing number of cars, it becomes necessary to improve existing and implement new methods of management of used tires. Nowadays only a few methods are in use. In European Union 40% of used tires are landfill, 20% energy recovery, 18% material recycling, 11% rethreading and 11% are exported [1]. Scrap tires are mostly disposed of in open or landfill sites are generating waste in natural environment which also can cause dangerous situations, like setting fire [1]. In Poland, the most common way of disposal is burning tires in kilns. This method has got positive sides such as a high calorific value that provides a high combustion energy, but on the other hand this simple way does not reuse tires as material recycling. In addition combustion tires in kilns causes emission of greenhouse gases. Other method of recycling used tires is pyrolysis. This process is the anaerobic thermochemical decomposition of organic matter, which can be used as an alternative or complement to the combustion process. Pyrolysis process is known from ancient times when it was used for the production of charcoal needed for the development of metallurgy. This technology over the centuries, underwent constant upgrading and still the researches on new uses for emerging products are being conducted. Over the past few years, many laboratories around the world were conducting researches on the pyrolysis of polymeric materials, for example Kobe Steel in Japan, Tosco in the U.S., Pyrolysis in the UK, Ebenhausen in Germany and others [2].

Depending on the feedstock heating rate, reactor temperature and residence time in the pair process pyrolysis can be targeted to receive one of three preferred products: char, oil or gas. Pyrolysis process could be carried out at different temperature: at 400, 500, 600 and 700ºC and also in different gas atmosphere, like in nitrogen and argon. In this temperature the char residue from pyrolysis is about 43÷44% [2]. Char can be used as activated carbon or gas, and oil can be used as high calorific fuel for energy cogeneration. Experimental results show that theoretical value obtained from *thermogravimetric analysis* (TGA) for solid yield (40.7%) is different than the much higher value obtain in the process - 53.4% [2]. The pyrolytic oil obtain is a mixture of different organic compounds especially hydrocarbons from rubber degradation. Liquid fraction could be great source of energy the GCV (*Gross Calorific Values*) value is about 42 MJ/kg, and also the sulfur content is about 1% - it is within the European standard for heating fuels [2]. Use moderate temperature regime (300÷500ºC) producing mainly pyrolytic oil, while at high temperatures (500÷900ºC) is preferable to produce the gas [3, 4]. Roy [5] reported that pyrolysis product yields is 52.5 wt.% solid residue, 27.7 wt.% organic liquids, 13.3 wt.% pyrolytic water and 6.6 wt.% pyrolysis gas. Laresgoitti [2] performed waste tire pyrolysis in a bath reactor at different temperatures.

The main compounds of gaseous fraction are: CO_x and H_2S. Carbon dioxide and carbon monoxide come from the hydrocarbons, oxygenated organic compounds from tires such as stearic acid, extender oil, etc. Hydrogen sulfide came from the sulfuric acid and also from the decomposition of the sulfur links - crosslinking [2]. The lighter hydrocarbons are generated from polymers decomposition. Tires rubber contain mainly SBR, styrene - butylenes polymer, which causes that in pyrolytic gases are present short aliphatic hydrocarbons [2]. The figure with composition of the pyrolytic gases shows that amount of CO_x is increasing with temperature and is the biggest in 700ºC, another gas compounds like H_2S, total C_1, total C_2, total C_4, total > C_4 have got similar level in temperature of 500÷700ºC. That means the best temperature, to produce maximum gas compounds, is higher than 500ºC.

The maximum concentration of gases occurs about 21÷31.5 minutes from start of process in 400ºC, that means that the gaseous fractions are generated in first part of process. Authors [2] described that low heating rate like 15ºC/min and temperature in the range of 400÷500ºC causes the best production of gaseous products. In others publications are solution for the gas cleaning by the distillation column [7]. Final product has got 70.5% of light hydrocarbons (C_1÷C_5), 8.5% of hydrogen, 14.7% of inert gases (like nitrogen, carbon dioxide, water vapor), 6.3% carbon monoxide and 0.0003% of hydrogen sulfide [7]. Combustion gaseous fraction after distillation process could generated 3.2 MW of power and the GCV is about 39 MJ/kg. In another investigation it was measured that in heat exchange equipment streams 2171 kg/h of gas fraction at 600ºC and energy $8.462 \cdot 10^5$ kJ/h [8] can be produced. Kyari [6] in pyrolytic liquids obtained from pyrolysis used car tires obtained mainly aromatic and aliphatic compounds such as alkylated benzenes, alkylated naphthalenes, alkanes and alkenes. They reported that oil contain ethyl-, propyl-, butyl-, pentyl-, hexyl- and heptylbenzene and ethenyl-, propenyl- and butenylbenzenes in high concentration. The aromatic compounds and VOC are generated in large amount in the process carried out under nitrogen and carbon dioxide atmosphere. Iron scrap, carbon from tires and high temperature in process causes the production of high value of carbon monoxide from the reduction of the carbon monoxide [8]. Description of the reaction scheme of pyrolysis process is very difficult or sometimes even impossible. Decomposition of polymers are very complicated process and could give a lot of various solution; it depend on temperature, pressure, flow gas, heating rate and others [8].

Main compounds of tires are polymers like polybutadien, *styrene-butadiene rubber* (SBR), polyisoprene, natural rubber. In the pyrolysis of tires and other polymeric products hydrocarbons in liquid and gas products are obtained. These products are reusable so we can recover energy, use them as fuel, or in the production of chemical compounds [2]. Pyrolysis in contrast to other techniques of tire management is a technique not requiring separation of the individual materials making up the tire (metal and material gain), which is much easier lowering investment costs. Additional benefits of the implementation of this technology is lowering the amount of landfilled waste, the recovery of chemical energy and consequently, reduced consumption of oil resources [9].

This process is not hazardous for environment. The literature data shows that the main components of pyrolysis gas from the car tires are carbon monoxide, carbon dioxide, hydrogen sulfide, and light hydrocarbons like: methane, ethane, ethene, propane, propene, butane, butene and butadiene, their calorific value is about 30÷50 MJ/m^3 [2]. Such a high calorific value allows and even forces the use of gas as an energy source.

Often the analysis of samples described in the literature, took place with a large time delay from the procurement and sampled the former badly stored. This article contains the results obtained from the analysis of gas samples. Then the checks of tire pyrolysis impact on the surrounding environment were made out.

Pyrolysis process/installation

The samples were fetched from the installation for pyrolysis of used tires. A few working installations exist now in the European Union. Installation in Figure 1 is located in southern Poland and the owner is PHU-GMG. This pyrolysis process was not continuous, but periodical. Five reactors allow almost continuous work. When pyrolysis process in the first reactor is finished, it is run in the second and in the other reactor it is cooled and so on. This installation is environmental friendly because of the leak-tightness of the equipment, and the process of used tires utilization. Tires are not burn but they are put into thermal degradation without the oxygen. This kind of utilization is a good way to reuse waste tires. In this process we get a fuel with a gross calorific value, gas and char which can be used as a filler. Output is maximum 1500 dm^3 per twenty-four hours and to 2.2 Mg (tons) of char. Maximum tires use in this process is 5 Mg (tons) per day, this comes from the capacity of the reactor which is 2.3 m^3 and when we use five reactors in one process we have 11.5 m^3. The pressure on the process is about 0.2÷0.4 bar (~ 1 atm).

The installation consists of several elements, connected by appropriate piping installation. The first element in Figure 1 is a reactor (1) set on the furnace used to heat the reactor. Another element of the line is the rectifying column (2), which is formed during the processes occurring in the reactor where gas mixtures of steam and water are separated, gas is distributed to liquid fractions. The next object is a line of low-pressure gas tanks: input (3) and output (3), along with the band filters placed between them.

Pyrolysis of whole tires is carried out in a furnace with a heating chamber at a temperature of about 370÷400°C. Such conditions ensure the achievement of the maximum amount of pyrolytic oil while reducing the weight of residual carbon and gas fraction [10]. When the temperature is growing up in the process, the amount of gas will be also increasing, due to the fact that the most volatile fractions of liquid pass into the gaseous state [7].

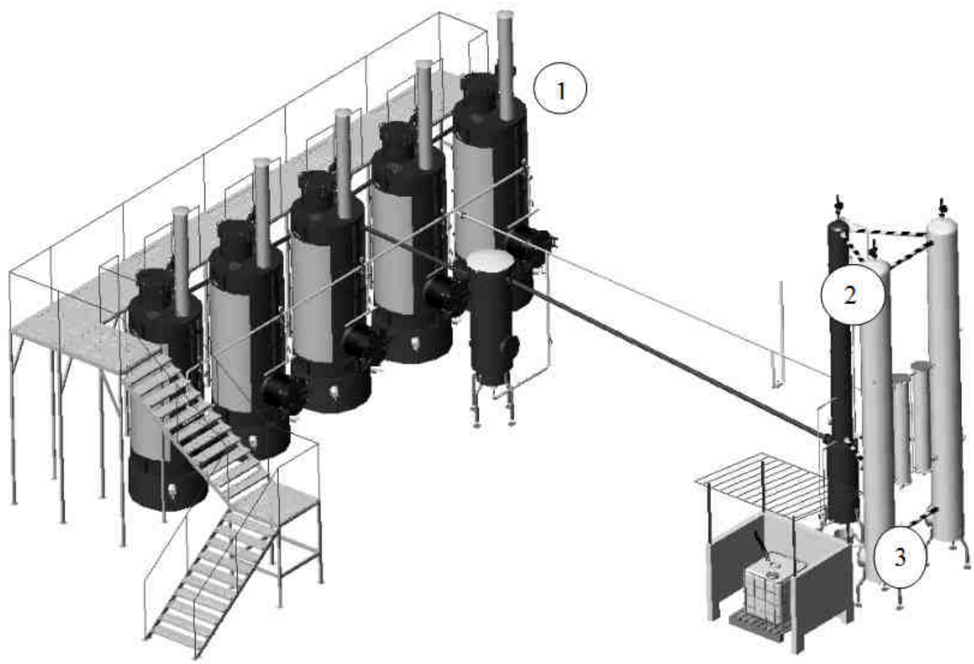

Fig. 1. Pyrolysis installation: reactors (1), rectification column (2), gas containers (3)

In tire pyrolysis the most advantageous are liquid hydrocarbons, which are raised in the process as much as possible, and steel is formed as a by-product. Gas products are used to heat the reactors, excess of gas can be burnt and it can be reused as heat or energy. The individual pyrolysis products are characterized by relatively high homogeneity, and therefore it is more advantageous to subject them to thermal processes than to the direct combustion of adjustment for energy [11, 12].

Currently only one reactor in closed pyrolytic line operates but the plan is to make continuous process line. The present technology provides for material recycling of whole used tires in a continuous manner by which obtained products are: pyrolysis oil, a mixture of hydrocarbons with different boiling points, therefore it is necessary to distillate the fractions (light, medium and heavy oil), char, gas, and steel scrap [13]. So far the whole process of material recycling of tires carried out in a pilot scale installation is not running continuously. A single reactor is equipped with a cooling system [13].

In contrast to the conduct of periodic processes in a continuous process, it reduces operating costs, since it keeps the pyrolysis at a constant temperature and constant pressure, reduces heat loss during cooling technological contributions and allows the optimization process, using the established collection system products [14].

Materials and methods

The raw material used for the pyrolysis were used tires. Tires where cut into 4 pieces, only to make it easier to load them into reactor. Elemental composition of the whole tires is 74.2 wt. % of C, 5.8 wt. % of H, 1.5 wt. % of S, 0.3 wt. % of N and 5.1 wt. % of O, the inorganic compounds like steel, fillers - 13.1 wt. % [2].

The samples are from the pyrolysis of used car tires of different brands. Samples came from different types of tires. Tire size ranged was from 14 to 18 inches. Analysis where performed on gas samples, which were collected from pyrolytic reactor into special Tedlar bags to store gas. Bags previously were flushed with inert gas to avoid the impact of the background on the results. Then the pyrolytic gas influence on the environment was checked.

Samples were taken from the chimney outlet and they were analyzed, furthermore the most volatile fractions of oil were determined. Outlet gases came from combustion chamber and also from reactor where the thermal decomposition was done. In this investigation the influence of emitted gases on the environment - atmospheric air - was checked. Samples were analyzed by gas chromatography using two gas chromatographs. The first is used to determine the composition of the hydrocarbon: Clarus 500, Perkin Elmer, equipped with a *flame ionization detector* (FID), Porapak-Q, 100÷120 mesh, 2 m long, 2.1 mm in diameter. Each time it was injected 200 mm^3 gas sample. The analysis was carried out at a constant temperature of 105ºC.

The second was used to determine the composition of inorganic compound. SRI chromatograph model 330 equipped with *thermal conductivity detector* (TCD), column 100÷120 mesh Shincarbon, 2 m long, 1 mm in diameter. Each time through the loop was dosed 1 cm^3 of sample. Initial temperature was 40ºC held for 6 minutes then 180ºC in a gradient of 25ºC/min held for 2 minutes. The test material came from two different installations and the results were compared.

Results

It is necessary to say that exhaust gas produced in the pyrolysis process is the only stream produced. Another products are like coal, steel and recoverable oil. Elemental analyses were done by CHNS analyzer. Sample of waste rubber and granulated tires were analyzed. In Table 1 the results from CHNS and GCV automatic analyzer are presented. The highest value is carbon which is in all hydrocarbons in polymer structure and the sulfur from cross-linking bonds between polymers and sulfur. Pyrolysis process could be carried out in different temperature and also in different gas atmosphere. The main products obtained from pyrolysis are: solid, liquid and gas. Proportions of products depend of pyrolysis parameters like: temperature, pressure and gas presence. In Figure 2 the results obtained by Laresgotti [2] in different temperature and presence of nitrogen are presented. Fractions of oil samples of were distillated under 100ºC. The test samples of light oil fractions were found to contain aromatic hydrocarbons: benzene, toluene, xylenes, and aliphatic hydrocarbons such as heptane, octane, pentane and styrene (Tables 3, 4). Analyses were made using a gas chromatograph equipment with a FID detector. The results obtained for samples of different installations were similar to each other. Identified compounds (benzene, toluene, xylenes) belong to a group of carcinogens. Therefore, it was made only qualitative analysis, the percentage of the individual compounds is not known. In addition, it should be considered that this oil fraction is not a stream of the process. It is the lightest (volatile) fraction of liquid products which is recovered and used as heating fuel. Gases from the installation which can influence the atmospheric air do not include benzene, toluene and xylenes.

Gas fraction contain mainly aliphatic compounds such as methane, ethane, ethene, propane, propene, butane, butene, pentane, pentene and oxides like carbon monoxide, carbon dioxide, hydrogen sulfide. In light oil fraction the content of benzene, toluene, etyltoluene, (*m*+*p*)-xylene, *o*-xylene is less than 2 mg/m^3. The research was carried out with a use of PB-070-2004-IE standard. The content of aliphatic hydrocarbons is beyond 1 mg/m^3 (method of research: EN ISO 9377-2:2003; PB-047-2004-E). In installation described by Arion [8] used for tyre pyrolysis at 500÷900ºC the examination of unburnt gases showed detection of 13 mg/g of benzene, 10 mg/g of toluene, and about 2 mg/g of ethylbenzene, *m*+*p*+*o* xylenes. Moreover it was found that in the process carried out at 900ºC PAH or BTEX were not identified [8].

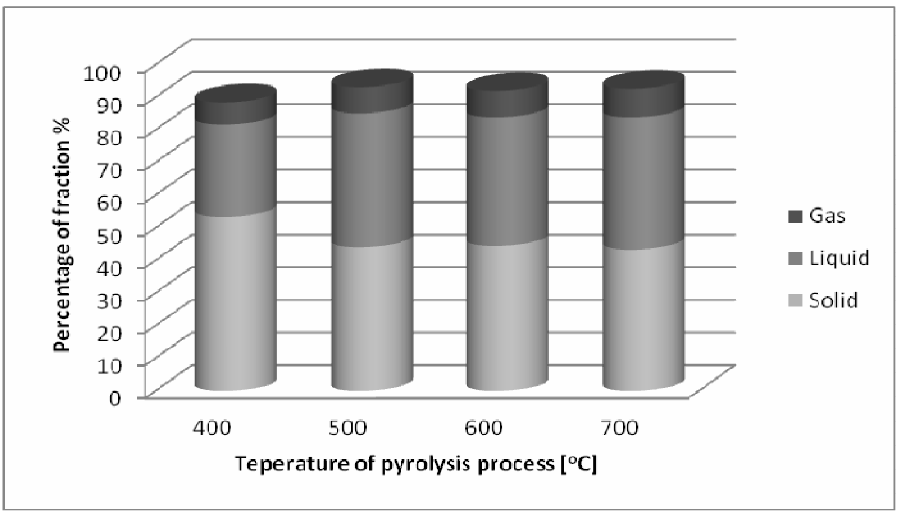

Fig. 2. Products from pyrolysis process obtained in different temperature [2]

Table 1
Elemental composition [wt. %] and gross calorific value (GCV) [MJ kg^{-1}] of the tire and waste rubber (determined by CHNS and GCV automatic analyzer)

Element [wt. %]	N	C	H	S	GCV [MJ kg^{-1}]
Rubber waste	1.2	79.9	7.4	1.1	41.9
Waste tires	0.7	82.0	7.1	1.9	-

In Table 2 the results of the gas research are presented. The main compounds of pyrolytic gas are hydrogen, carbon monoxide, carbon dioxide, and methane. GCV of the pyrolytic gas in 400°C is 81.6 MJ/m^3 and it is decreasing with the highest temperature in 700°C is 69.5 MJ/m^3 [2].

Table 2

Main compounds of pyrolytic gas

	Concentration [%]	**Concentration [%] [102]**
H_2	9.3	-
CO	47	14.2
CH_4	12.7	-
CO_2	26	55.2
SO_2	-	1.3
Total VOCs	-	8.9

Table 3

Tentative GC/FID characterization pyrolytic gas from car tire pyrolysis

Retention time [min]	**Tentative assignment**	**Peak area [%]**
0.73	Methane	17.77
1.35	Ethene	8.82
1.60	Ethane	9.55
3.89	Propene	9.68
4.29	Propane	6.10
11.58	Isobutane	28.98
10.98	Butane	3.13
17.38	Pentene	3.15
18.07	Pentane	7.38
Total identified		96.56

Table 4

Tentative GC/FID characterization of pyrolytic liquids fraction under 100°C from car tire pyrolysis

Retention time [min]	**Tentative assignment**
2.65	Pentane
6.3	Benzene
16.03	Toluene
20.71	*p*-xylene
25.30	Limonene

Conclusions

Experiment allows to understand better the mechanism of depolymerization which causes production of gas phase. The laboratory equipment allowed gas compound detection in analysis samples. Compounds which are detected in samples, where formed in high temperature. Degradation of tire rubber polymers includes a lot of processes like: polymerization of alkynes, polymerization of olefins, diolefins, then cracking, Diels-Adler's cycloaddition and aromatization, dehydrogenation into olefins, diolefins, finally alkynes, condensation of aromatic compounds, methane, hydrogen formation [8].

Carbon dioxide and carbon monoxide contained in the pyrolysis gases is likely to come from the decomposition of organic compounds containing oxygen in its molecule, such as stearic acid, fillers, oils, etc. Hydrogen sulfide is formed from sulfur bonds releasing the cross-linking of polymers during the vulcanization of rubber. The sulfur content in the tire is about 1.5 wt. % [1]. The amount of hydrocarbons containing less than 5 carbon atoms per molecule (< C5) is by far the largest in the product gas and prevails over the other compounds. The source of light aliphatic hydrocarbons is the depolymerization of styrene butadiene (SBR), and other organic polymers, which are part of the tire.

The proposal, which comes from the analysis of the results is the need to maintain integrity of the apparatus. Pyrolysis gas is very dangerous, and its main ingredient (47%) is extremely toxic carbon monoxide. The simplest hydrocarbons such as methane, ethane, propane, butane, which also form part of the gas fraction are supposed to be recycled to the combustion chamber, where the combustion-used to maintain high process temperatures are transformed into carbon dioxide and water vapor (a few water). In the absence of protection apparatus when receiving the most volatile fraction of oil in a distillation column aliphatic hydrocarbons may be broadcast. It is necessary to avoid emission of PAHs, not destroyed gases, which can be dangerous. Hermetic reactor could not pose a threat to the environment and health of workers handling the installation.

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GAZOWE PRODUKTY PIROLIZY OPON SAMOCHODOWYCH

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Abstrakt: Zgodnie z dyrektywami obowiązującymi w krajach należących do Unii Europejskiej, zużyte opony samochodowe powinny być w 75% poddawane recyklingowi. Najbardziej popularną metodą zagospodarowania opon jest ich spalanie w cementowniach, jednakże sposób ten nie wykorzystuje w pełni zasobów energetycznych zużytych opon. Proces pirolizy jest alternatywnym rozwiązaniem. Przeprowadzone badania miały na celu sprawdzenie wpływu zarówno procesu pirolizy, jak i lotnych produktów pirolizy (gaz i lekka frakcja olejowa) na środowisko. Próbki analizowano przy użyciu chromatografu gazowego. Wnioski, które sformułowano po analizie wyników, to m.in. konieczności hermetyzacji i kontroli szczelności reaktorów, w których przeprowadzany jest proces pirolizy. W lekkiej frakcji olejowej wykryto lotne związki wielopierścieniowych węglowodorów aromatycznych, natomiast w gazach odlotowych nie wykryto BTEX (benzen, toluen, etylobenzen oraz ksyleny) oraz wielopierścieniowych węglowodorów aromatycznych.

Słowa kluczowe: piroliza, opony samochodowe, utylizacja, produkty gazowe