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ENVIRONMENTAL SAFETY TECHNOLOGY ON SCRAP TIRES TREATMENT

This article is devoted to the problem of scrap tires treatment. The appropriate technology of tires pyrolysis and physical-chemical analysis of liquid hydrocarbons, which are usually obtained in the process of thermal destruction of wastes are considered. Main aim of this analysis is the comparison of liquid fraction characteristics with traditional fuels (petrol, diesel, kerosene) in order to show that this pyrolysis product could be identified like an alternative motor fuel.

Присвячено проблемі переробки зношених шин. Описано технологію піролізу шин. Проведено аналіз фізико-хімічних властивостей рідких вуглеводневих, які зазвичай отримують під час термічного розкладу відходів. Розглянуто результати порівняння параметрів рідкої фракції з традиційними паливами (бензин, дизель та мазут), який доводить, що продукт піролізу можна визначати як альтернативне моторне паливо.

alternative energy carriers, pyrolisys, tires, utilization, waste treatment

Introduction

The question about alternative energy sources is prior for most developed countries all over the World in the condition of crude oil deficiency and depletion of natural resources.

There is one basic foundation tendency of world development, which envisages a gradual transformation of human activity character from the biggest fuel-energy resources consumer to effective their producer [1].

Basic advantage of renewable energy sources is concentrated in the assertion that their using doesn't change an energetic balance of the planet and helps to solve global human goals in energetic and ecology. These facts explain why renewable energy sources have a great development abroad and show optimistic forecasts about their future implantation.

In the nearest future, taking into account a level of acuity problem, an attention of business circles over the whole world will be concentrated on this perspective economics segment. The global character of ecological situation, alternative-less rescue from impendent catastrophe, actuality, necessary innovation make this sphere of industry more attractive from the commercial point of view.

Instead of greedy suck up of natural resources, thoughtless throw and production of numerous wastes garbage a mankind is obliged to make an actively changes of traditional energy carriers (completely or partially) by energy obtained untraditional methods, including waste treatment.

Waste treatment was recognized as an important part of energy-saving policy. All ways of energy saving foresee both implantations of technologies, which increase an effectiveness of traditional energy use and re-orientation of energy balance due to using of alternative energy carriers after waste treatment [2].

Scrap tires as a significant capacity source of raw materials

Among all diversity of human life remains, scarp tires and also other rubber products are considered as unique wastes: depending on waste management system and used recycling technologies received secondary materials can be both in the form of rubber powder or energy carriers. Such varied properties of scrap tires become apparent thanks to their composition.

Since automobile tire should be stand to extremely loads, the tire consists of high quality materials (about 15 pcs.). Tread, side walls and rim place are manufactured from the special rubber mixtures. Nylon, steel or\and kevlar (synthetic fiber instead of steel) are used as a basic strengthener. Carcass basically consists of viscose silk or complete polyester, interior of rim place – from steel [3].

When tire is replaced from a wheel rime there are a lot of reasons why it can be turned into scrap tires: finished term of exploitation, worn tread, un-repair damages or it was changed by a new one. And if a new tire has a fixed price, then scrap tire has no value. Unfortunately, this opinion is peculiar to most people.

Actually scrap tires are a valuable source of useful secondary materials. And effective tires recycling will provide both decreasing of anthropogenic loading on the environment and give a chance to shorten using of primary natural resources due to obtained secondary materials.

Nonrenewable character of natural crude oil forces to use the secondary resources with maximal efficiency, that in place of waste stacks one should develop and inculcate the new sphere of industry – commercial processing of amortized tires.

World practice shows that scrap tires treatment is able to provide the effective decision of the problem accumulation in economically advantageous ways. The most widespread methods of tires utilization are incineration with the purpose of obtaining energy (most popular is incineration of tires in cement stoves), pyrolysis under low or high temperature obtaining distillate, rubber crumb and powder, which are used for making polymeric mixtures and construction materials. Each of the mentioned methods is rather actual depending on the ultimate goal of utilization, inasmuch as every method implies obtaining different products.

A particularly desirable way to dispose used tires is recovery of hydrocarbons and carbonaceous materials from them. To all appearance the hydrocarbons may be use as fuel source replacing expensive light oil products.

To extract secondary oil products from scrap tires different pyrolysis systems are commonly used. Pyrolysis is a well known process with a number of different terms, including a gasification, devolitization, destructive distillation, thermal depolymerization, thermal cracking, carbonization and coking [3]. Under the influence of temperature at the absence of oxygen scrap tires are separated into solid, liquid and gas substances. At that long polymeric links are changed into hydrogen molecular parts.

Environmentally safety technology on pyrolysis of scrap tires

There are a lot of different systems and technologies for utilization of scrap tires by pyrolysis method. All of them are different by structure of processing lines, but all of them have a same goal: to obtain a liquid fuel, carbonaceous materials and gas [4].

Pyrolyse system, which was used for producing the investigated liquid hydrocarbon fraction, has been taken into consideration because of many disadvantages of the previous developed pyrolyse processes and apparatus, and also has other numerous advantages that will be apparent to those skilled in the art.

Broadly, the process of the presented system produces liquid and gaseous hydrocarbons from rubber under the influence of certain temperature and pressure. It includes three principal sectors: preparation, pyrolyse and finish sectors.

A preparation sector implies a previous treatment of scrap tires before the procedure of pyrolysis.

The second sector is symbolically called pyrolysis sector, which is a heart of the present invention. It is a main instrument to transform UNNEEDED scrap tires into valuable secondary products - liquid hydrocarbons and solid carbonaceous materials.

This sector consists of two well-sealed reactors, where the procedure of pyrolyse takes place, erect condenser to convert a pyrolytic gas into liquid fuel, reservoirs to collect the liquid fuel and gas, and condensing columns to make a re - condensation of the rest of gases.

Using two well-sealed reactors is not an idle idea, this solution was significantly grounded on the principle of energy saving.

Energy saving principle implies usage of rest heating from first reactor to heat the second one. It means that it is necessary to waste less energy to heat the second reactor (according to calculated data, it saves about 30% of energy).

Separately the temperature of the pyrolysis process should be marked.

Moreover, temperature influences the quantity of products obtained. This technology is based on a principle of low temperature pyrolyse which is characterized by maximum output of liquid and solid products with minimal quantity of pyrolytic gas that has a maximal calorific value.

Well-sealed reactors exclude any extra limited emissions into atmosphere.

The third sector is final. It is assigned to treat a solid rest, which is rich in carbon black, and also scrap metal.

Including apparatus to treat a solid rest it allows excluding secondary wastes as a whole turn all products into obtaining maximal quantity of secondary valuable goods.

Apart of ecological constituent, finish sector is a real source of additional money, as carbon black, which is finally obtained, is of high demand in the market. Carbon black is widely used in roof coating, asphalt, low-pressure hoses such as those used in the automobile industry, paints as fillers and as bonding agents, plastics as fillers and as bonding agents, ink, waste treatment filters, off road tires and marine coating for use on docs, bridges, boats, etc [5].

Energetic capacity of the considered technology on scrap tires treatment can be achieved 85−90 % of ready-to-use energy carriers: liquid hydrocarbons (aprox. 40 %), gas (aprox.20 %) and solid rest (aprox. 35 %).

Using of pyrolytic gas doesn't differ from the using methods for traditional natural gas: part of obtained gas is used for production needs, and the rest − to direct consumers. Calorific value is about 27 MJ\kg.

Solid carbonaceous rest can be used like a qualitative substitute of natural coal. It consists of carbon (~ 80 %), soot (10−15 %) and sulphur (3 %). Calorific value is about 29 MJ\kg. It's widely used as a fuel element for kilns and boilers, sorbent for filtration of sewage from industrials or solid stove fuel.

Liquid hydrocarbons are identified like an alternative motor fuel according to physical-chemical characteristics. Given alternative energy carrier is a perspective substitute of oil fuels, obtained by traditional methods.

It looks like an oily liquid with dark-brown color and character oil odor. Calorific value is about 39 MJ\kg. This value (and also many others) testify about proximity of this pyrolysis secondary product to oil derivatives: calorific value of oil is about 41 MJ\kg and calorific value of petrol is about 42 MJ\kg.

Without any chemical-technological treatments this liquid fraction can be recommended to use instead of natural gas on boiler plants. Also it should be noted that according to the calorific value, 1 kg of this liquid hydrocarbons equals to 1,88 m^3 of natural gas.

Analysis of physical-chemical characteristics of pyrolysis liquid hydrocarbons

To identify that liquid hydrocarbon can be used as an alternative motor fuel there were done a series of laboratory investigations to determine physical-chemical characteristics of liquid fraction and compared with traditional oil fuels. All tests were carrying out on the equipment of chemmotology test center at the National Aviation University (Ukraine).

Taking into account that composition structure of investigated liquid fraction is similar to composition of crude oil, that's why it could be investigated by the same methods. Close authentication allows the comparing of this fraction with oil derivative.

Hydrocarbon fraction of scrap tires pyrolysis is enough complex mixture with variable composition, its composition and properties can be changed under the following conditions:

− if during the pyrolysis process all necessary conditions (temperature regime and pressure) were not controlled and changed arbitrary;

− if a storage conditions are not constant.

Properties of secondary products also depend on tire manufactures and their rubber mixtures secrets. But this fact is negligible small, therefore it's ignored.

Physical-chemical characteristics of obtained product have important meaning in correlation of its composition and marketable properties. They are density, viscosity, ignition point, temperature of solidification and also fractional composition.

Density belongs to most spread investigated parameter for oil and oil products. Its value depends on many factors: chemical nature of compounds, fractional composition, and quantity of tarry matters, or solved gases, etc. Using density value it is possible to make an approximate conception about composition of analyzing product as this value differs from one to another group of crude oil [6].

Tested samples (SAMPLE 1 and SAMPLE 2, which was took away from different lots) had a different density value. It confirms that during pyrolysis process there was a disruption of technological requirements. That's why it is necessary to investigate the most appropriate technological conditions to obtain a maximum quantity of valuable light products. In the SAMPLE 2, which has lower density, it was allowed to obtain higher quantity of light oils (aprox. 8 % ↑).

All results are given in the tab. 1.

As a recommendation, it is necessary to test a density for every lot with the aerometer to be sure about quality of product.

Like other characteristics, oil viscosity is closely connected with chemical composition of product. It is determined by forces of intermolecular interaction, with the increasing of which a viscosity increases too.

Viscosity is changed within a wide limits (from 1,98 to 265,90 mm^2\s), and is defined by fractional composition and temperature [7].

Within the laboratory a viscosity was tested at 20 ºC and 100 ºC. Viscosity value of SAMPLE 2 is verified that there is a higher content of light fractions in comparison with the fist one tab. 1.

Ignition point is also important value for any fuel product, as it is determines a minimal temperature, at which oil vapors form with air a mixture. In turn this mixture is able to make a short-time flame at the presence of outer fire or spark. This character shows temperature at which oil product becomes inflammable [8].

Regarding to tested samples, the ignition point was determined in a closed crucible. SAMPLE 1 showed ignition point about -4 ºC while SAMPLE 2…-17 ºC. Such impassive difference is the evidence about different content of light fractions.

Table 1

Physical-chemical properties of liquid hydrocarbons

Parameter	SAMPLE 1	SAMPLE 2	Test methods
Density at 20 ºC, kg/m^3	928	882	GOST 3900 – 85
Viscosity kinematics, mm^2/ s			
at 20 ºC	8,40	1,85	GOST 33 – 2000
at 100 ºC	1,39	–	GOST 33 – 2000
Ignition point in closed crucible, ºC	- 4	–	GOST 4333-72
Solidification temperature, ºC	- 29	-65	GOST 20 287-91
Water content, %	0,1	1,5	GOST 24 77-65
Sulphur content, %	1,65	–	GOST 19121
Fractional composition, ºC:			GOST 2177-99
$T_{пк}$,	71	73	GOST 2177-99
10 %	166	117	GOST 2177-99
50 %	284,5	182	GOST 2177-99
76 %	355	–	GOST 2177-99
80 %	–	338	GOST 2177-99
86 %	–	357	GOST 2177-99
$T_{кк}$	355	357	GOST 2177-99
General volume of distillation, ml	76	88	GOST 2177-99
Rest at retort, ml	18	11	GOST 2177-99
Loss, %	2	1	GOST 2177-99

At the lowering of temperature a part of oil components is become more viscous and slow-moving. This property noticeably complicates any marketable-transport operations and exploitation under temperatures. It is called as solidification temperature [9].

Solidification temperature for the first sample was within – 29 º C, at that time for second sample it was – 65 º C.

Fractional analysis is an important value in estimation of oil quality. At the atmospheric pressure and temperature increasing there is evaporation of different individual hydrocarbons – fractions, every of which is boiled away at the certain temperature interval. Fractions, which boil away under 350 º C are called as light distillates [10].

In the tab. 2 below a boiling temperatures, at which a traditionally accepted oil fractions boil away are undicated:

Table 2

Generally accepted oil fraction

Fraction	Temperature boiling, °C
Petrol	35–205
Fuel for reactive engines	120−315
Diesel fuel	180−260
Gas-oil	230−360
Black oil	< 350

Fractional composition determination of the samples showed that they differ by the different content and volume of fraction. All results are reflected on the tab. 1.

Water is a mineral addition in the oils; its presence is unwanted in any oil product according to technical norms. In the process of cooling, ice crystals which stop up fuel filters are formed; in the process of heating a vapor which leads to explosion is formed. That's why water has a complicated oil treatment and a negative influence on functional properties of oil products [11].

Water presence in the tested samples is unstable indicator: during storing of this pyrolysis product the water quantity is increasing. Laboratory tests showed not a great water content, however it's necessary to use a stabilizers to prevent a water formation.

Regarding to sulphur content it's a main heteroelement which is present in the oil products, its concentration can changed from hundreds percents to 6−8 %, in some cases to 9 % or even 14 %.

Unfortunately, the investigated samples showed enough high sulphur percent, that's why it's recommended to clean any pyrolysis products from suplhur by the known chemical-technological methods [12].

So, realized analysis showed that there is no complete coincidence of liquid fraction with the properties of traditional motor fuels, but approaching to the parameters of oil products make these liquid hydrocarbons a perspective to use like a synthetic motor fuel in the condition of additional chemical-technological treatment to the existing parameters.

Taking into account an ecological, economics and energetic rectangular components of the pyrolysis process and obtain of synthetic energy carriers liquid hydrocarbons will stay a valuable kind of non-oil fuel today and in the nearest future it will leave .

Conclusion

1. World community consider using of alternative energy sources as a perspective way to solve increasing problems of energy supply. Availability of non-exhaustible raw materials (different types of waste) and ecological purity of advanced engineering technologies are determinant advantages in the conditions of natural organic fuel resources depletion and towering rate of environment pollution.
2. Scrap tires are powerful source of raw materials for production of alternative energy carriers, including synthetic motor fuel. In view of their unique composition it is possible to obtain three effective energy carriers: gas, carbonaceous materials and liquid hydrocarbons. At the same time scrap tires are dangerous for environment and living organisms. Therefore effective solution of their treatment should contain both economics grounds and ecological advisability. There are a lot of different technologies in thermal treatment of scrap tires. Each of them propose actual technological implantation and solution for utilization of tire wastes. Considered technological system has presented a realization of moderate achievement of science and is both environmental safety (excluded formation of secondary wastes or discharge of pollutants into atmosphere) and economic defensible (all obtained products are in demand and are competitive in the market).
3. Fraction of liquid hydrocarbons is determined as perspective replacer of traditional motor fuels. Although its properties don't correspond completely to traditional motor fuels, but additional chemical-technological treatment will provide a finishing up to existent standards. This type of alternative fuel will become a valuable synthetic energy carrier for many years forward, for the present time of automobiles.

References

1. *Девянин С.Н.* Растительные масла и топлива на их основе для дизельных двигателей / С.Н. Девянин, В.А. Марков, В.Г. Семенов. – Х.: Новое слово, 2007. – 452 с.
2. *Суходоля О.М.* Роль та місце енергозбереження у забезпеченні енергетичної та національної безпеки / О.М. Суходоля // Ел. журнал «ЕСКО». − №8. – 2003.
3. *Shulman* Valerie L. Tire Recycling after 2000: Status and Options / Valerie L. Shulman, ETRA Publications, 75116 Paris FRANCE, 2000.
4. *American* Society for Testing and Materials // Standard Practice for Use of Scrap Tires in Civil Engineering Applications, Standard Method D 6270-98. − Vol. 09.02, ASTM. − West Conshohocken, Pennsylvania, 1998.
5. *Blumenthal M.* Report of the Scrap Tire Management Council / M. Blumenthal, J. Serumgard. − Amsterdam, 1998.
6. *ГОСТ 3900-85.* Методы определения плотности. − М.: Изд-во стандартов, 1985.
7. *ГОСТ 33-2000.* Определение кинематической вязкости и расчет динамической вязкости. − М.: Изд-во стандартов, 2000.
8. *ГОСТ 4333-72.* Метод определения вспышки и воспламенения. − М.:Изд-во стандартов, 1972.
9. *ГОСТ 20 287-91.* Метод определения температуры текучести и застывания. − М.: Изд-во стандартов, 1991.
10. *ГОСТ 2177-99.* Метод определения фракционного состава нефтепродуктов.− М.: Изд-во стандартов, 1999.
11. *ГОСТ 2477-65.* Метод количественного определения содержания воды. − М.: Изд-во стандартов, 1965.
12. *ГОСТ 19121.* Определение серы ламповым методом. − М.: Изд-во стандартов.

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