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IMPROVING OF ECOLOGICAL CHARACTERISTICS OF TECHNOLOGY ON PYROLYSIS OF SCRAP TIRES

This article is devoted to the problem of looking for new alternative energy sources. Mutually beneficial integration of alternative energy searches with utilization of scrap tire is considered. Concerned processing line on scrap tires treatment is environment friendly and economically sound.

Наведено інформацію про пошуки альтернативних джерел енергії. Описано взаємовигідне поєднання процесу пошуків альтернативної енергії з переробкою відпрацьованих шин. Розглянута технологічна система для утилізації зношених покришок є екологічно виправданою та економічно доцільною.

Introduction

Worsening mountain and geologic conditions of hydrocarbon materials mining, toughening the ecological norms, unstable situation in the oil market – all these facts make us looking for new alternative energy sources. It is not so difficult to forecast that already the next decade a growing volume of fuel and energy will be provided due to energy saving methods.

The definition "energy saving methods" foresees both the inculcation of technologies, which increase the effectiveness of using traditional energy carriers and diversification of energy balance due to using alternative energy sources. This implies that the effective energy saving policy is a guarantee of economical growth and stable development of country as a whole [1].

The idea of alternative fuel application, which first appeared during the oil crisis in the USA in 1970, starts to spin up nowadays. In those years this problem was solved thanks to oil price stabilization, as the oil volume was enough to satisfy the needs of people around the world. Nevertheless, today this situation has changed: according to the forecast of scientists, the world oil reserves are enough for few decades only. Therefore, the World Energetic is experiencing substantial structural changes, connected with predicted decrease of oil production by leading manufactures.

The definition "alternative sources of fuel and energy" has deeper meaning in comparison with a simple conception of development and inculcation of the "alternative" methods and technologies. To provide the effectiveness and advisability of any "alternative" project, it is necessary to integrate such project with environmental protection [2].

Namely, the main flow of investments are directed to inculcation of projects, which superpose the receiving of alternative energy carriers with utilization of accumulated wastes. This integration is mutually beneficial both from economic and ecological points of view. "Waste energy" is a rational well-grounded solution for future generations.

To understand the above-mentioned assertion, it is necessary to consider the problem of scrap tires accumulation.

Scrap tires as a significant capacity source of raw materials

Scrap tires are high capacity and continuously accumulated source of hydrocarbon materials, which imperil a high danger for human health and life and surrounding environment as a whole.

According to the data, sounded at the U.N.O. Conference on environment and development (Rio de Janeiro, 1992), volume of solid waste will increase 4-5 times up to 2025. At the same time, the world volume of scrap tires makes 25 million tons with year-by-year increase in seven million tons. In Europe, the total volume of accumulated scrap tires is three billion pieces (around two million tons). In the USA about 280 million used tires are accumulated annually, and their total volume exceeds two billion pieces [3].

Concerning treatment and utilization, only 23 % of used tires are reused after wear and tear, namely through export to other countries, incineration to obtain energy, mechanical fragmentation for road building and others. The rest 77 % of scrap tires do not find their post-life application.

Regarding Ukraine annual accumulation of scrap tires is 0,74 million tons. Only in Kyiv region the used tires growth make 100 thousand scrap PKW tires and 65-70 thousand LKW scrap tires.

About 2 % of amortized tires are incinerated; about 1 % - retreaded and is brought back to exploitation stage. The rest are taken to the waste disposals, ravines and suburban forest belts. Such behavior and attitude to scrap tires lead to worsening of critical ecological situation in Ukraine.

Although Ukraine does not feature the list of the countries with great indices of scrap tires accumulation, but in the nearest future the intensive automobilization could lead to creating vast garbage of wastes with high concentration of polymers.

Essential reasons why it is necessary to treat scrap tires

In addition to sizeable accumulation of scrap tires on the ground, they have a direct impact on human health and all living world around.

First of all tire piles are excellent breeding grounds for mosquitoes, insects and rodents. Because of the shape and impermeability of tires, they may hold water for long periods providing sites for mosquito larvae development in particular. Such neighborhood within housing estates will cause rising of infection cases among inhabitants. Most of infections from rodents and insects may have dramatic consequences for children and adults.

Regarding tire burning, there is virtually no possibility of spontaneous combustion of tires in wastes. However, once fully ignited, a tire fire is difficult to extinguish. Fire can endure for weeks or months, depending upon the volume of tires. A tire fire creates dense, oily smoke, which can be carried to great distances, impairs visibility, and soils painted surfaces. Toxic gas emissions include polyaromatic hydrocarbons, CO, SO_2, NO_2, and HCl. Heat from tire fires also causes some of the rubber to break down into an oily material. Prolonged burning increases the likelihood of surface and groundwater pollution by the oily material. Emissions from open tire fires may be more toxic than emissions from an incinerator, regardless the type of fuel. Airborne emissions from open tire fires can have a serious impact on health and environment. Open tire fire emissions include "criteria" pollutants, such as particulate, carbon monoxide (CO), sulfur oxides (SOx), nitrogen oxides (NOx), and volatile organic compounds (VOCs). They also include "non-criteria" hazardous air pollutants, such as polynuclear aromatic hydrocarbons (PAHs), dioxins, furans, hydrogen chloride, benzene, polychlorinated biphenyls (PCBs); and metals, such as arsenic, cadmium, nickel, zinc, mercury, chromium and vanadium.

The emissions from an open tire fire may pose significant short-term and long-term health hazards to nearby persons. These health effects include irritation of skin, eyes, and mucous membranes, respiratory effects, central nervous system depression, and cancer [4].

Therefore the European Committee adopted a special directive “About garbage” on April 2, 1999, according to which scrap tires burn is prohibited since 2003.

Left on the garbage or buried in the ground scrap tires are not exposed to biological decomposition. Their contact with rainwater or underground water leads to washing out toxic organic substances: dihpenilamin, dibytulphtalat, phenantren, etc.

In spite of negative influence of scrap tires, they are valuable raw materials.

Rubber is a basic component of any tire. Taking into account the coefficient of wear a rubber part in scrap tire approximates 65 %. According to physical and chemical characteristics, rubber is a unique material because of its properties: it preserves elasticity after temperature treatment, it does not react with plentiful aggressive materials, and it is flexible at the high coefficient of wear. In combination with steel, aramid, polyamide or rayon tire cord, rubber shows itself as high-quality material.

All above-mentioned facts attest that scrap tires, which consist of rubber mainly, have a big potential of utilization. And depending on main goals of investor, who invests money into utilization projects, it determines how possibly in present economic conditions at the high use of potential of threadbare tire as valuable material again effectively recycle them economically. In other words, the most acceptable method for processing is easy to choose.

Nonrenewable natural crude oil forces to use the second 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 accumulation problem in economically advantageous ways. The most widespread methods of utilization of tires are incineration with the purpose of obtaining energy (most popular is incineration of tires in cement stoves), pyrolysis in conditions of 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 every method implies obtaining different products.

A particularly desirable way to dispose used tires is recovery of hydrocarbons and carbonaceous materials from them. The hydrocarbons may be use as fuel source replacing expensive petroleum products [5].

To extract secondary oil products from scrap tires 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. 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 [6].

Improving ecological characteristics of technology for pyrolysis of scrap tires

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

The processes and apparatus of the prior art have several disadvantages. They are generally not capable of producing liquid hydrocarbons having low sulfur content. As a result, the liquid hydrocarbons produced in such processes create high sulfur emissions when burned. Alternatively, the liquid fuel must be further treated to remove sulfur before being used as fuel.

Fuel also involves significant fire and explosion risk due to presence of oxygen during preheating or pyrolysis. Other drawbacks of the processes and apparatus of the prior art include the fact that they often produce high levels of emissions and secondary wastes. Some processes and apparatus also use dangerous catalysts.

Pyrolyse system, which is proposed for consideration, has been taken into consideration because of many disadvantages of the previous developed pyrolyse processes and apparatus, and also have other numerous advantages that will be apparent to those skilled in the art [7].

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.

Preparation sector implies a previous treatment of scrap tires before procedure of pyrolysis.

When scrap tires are unloaded from a truck, inspector makes a perfunctory inspection to reveal any mechanical contaminations (nails, stones, and glass) or dirt. Presence of dirt or any other contaminations inside the reactor will negatively influence the quality of products obtained and will reduce exploitation time of apparatus. In any case an owner will bear losses!!! Therefore, an application of water pump and air compressor are important necessity to provide a quality of secondary products and prolonged working time of reactors.

An essential advantage of this sector is an off-line control of the tire cutter, which divides a whole tire into four fragments. Procedure of tires fragmentation allows maximizing loading capacity of raw materials into the reactors.

The off-line control is an essential preference, as it is possible to transport the cutter directly to the garbage of scrap tires. Immediately fragmentation of tires on the garbage makes it possible to load a truck with more tires in comparison with a whole one.

Second sector is symbolically called pyrolyse 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 should be marked the temperature of the pyrolysis process. As it was investigated the temperature of sulfur gasification from rubber is about 432 ºC that implies application of temperature less than 432 ºC inside the reactor to produce a liquid fuel with low content of sulfur. Low sulfur fuel is ecologically friendlier!

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.

Finally, at the end of is a finish sector – the third one. It is assigned to treat a solid rest, which is rich in carbon black, and 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.

On the base of above-mentioned description of sectors there is a detailed draw of the whole below process step-by-step:

1) preparation of scrap tires to pyrolysis: reception, inspection, removing any mechanical contaminants or dirt;
2) filling rack with scrap tires fragments and loading into the first reactor;
3) heating rubber in the first sealed reactor at the temperature of about 127-440ºC under a pressure of about 759 mm Hg absolute for a reaction time sufficient to cause the rubber dissociation into a vapor phase and a solid phase;
4) removing some of the vapor phase from the reactor to produce a vapor stream;
5) condensing a vapor stream to produce low sulfur liquid hydrocarbons and remaining gaseous hydrocarbons;
6) re-condensing rest gases into condensing columns;
7) processing the solid phase to produce a solid carbonaceous material;
8) filling the second rack with scrap tire fragments and loading into second reactor;
9) pre-heating the second reactor by rest heat of the first reactor by means of pressure regulated valve;
10) other procedures are repeated being from the 3 point till 7 one.

As discussed above several products are produced by the present invention, such as fuel oil, methane gas, carbon and steel. Typically 50 % is reclaimed as fuel oil, which equals to approximately 3,79 l of fuel oil per passenger tire. Uses for such a fuel oil include all uses of standard industrial fuel. Power plants can use the fuel as a pre-treatment for coal, as an ignitor for coal, or as a primary fuel for firing their boilers. Small power plants that use diesel generators can also use the fuel instead of or in conjunction with diesel fuel. The fuel may also be used as home heating oil.

The gaseous hydrocarbons will comprise mostly methane gas. The methane gas can be used to fuel the burners of the present processing line, or it can be sold as a fuel source. Optionally, methane can be used to generate electricity and the electricity can be sold, or the gaseous hydrocarbon can be used to fuel co-generation unit so that steam and/or electricity can be sold.

The solid carbonaceous material that is a product of the present invention makes up approximately 43 % by weight of the originally used tires. The process will generally reclaim the carbon in the form of carbon black with moisture content below 1 %.

The fuel oil and solid carbonaceous product can be combined to produce an emulsion for use in rubber/asphalt mixes. Rubber/asphalt highways have been built in several locations around the United States and these roads have proven to be better than conventional asphalt roads. Until recently, the only form of rubber available for use in RA roads was crumb rubber, which is produced by grinding tires in small particles. Crumb rubber often has the steel and fiber normally found in tires contained within it. To process these particles an adhesive must generally be added to bond the crumb rubber to the asphalt. It must then be heated to high temperatures in order to melt the rubber into the asphalt and form rubber too. Problems generally occur throughout the application process. The steel and fiber clog small jets in spray equipment and this requires frequent down time and expensive repairs at the job site. The cost of crumb rubber varies widely but it is generally much more costlier than traditional asphalt.

Present emulsion of this processing line is the result of the memory between the fuel oil and the carbon black that causes them to develop a strong bond very quickly. The emulsion has a high viscosity, contains fine carbon powders, and can be easily mixed with asphalt.

The finished rubber/asphalt roadway is stronger, more flexible and more weather resistant than traditional roadways. In addition, traction is better and the roadway is quieter. Most important the emulsion is less expensive than the crumb rubber which is presently used in such rubber/asphalt roads.

Another product that is produced by the present processing line is steel. Steel typically makes up approximately 4 % by weight of each tire. Steel can be recovered and easily sold to local scrap metal markets.

Conclusions

It is obvious that nearest crisis of traditional energy carriers, their shortage will force looking for attractive and profitable alternative energy sources.
Wind or solar energy is a good solution, which has many advantages and disadvantages, though. However, there is a question emerging! Would it be rational to use "natural" energy, if there is a possibility to get a "waste energy" from solid wastes?
Therefore, such decision will help to decrease an anthropogenic loading on the environment, to make our surrounding more clear.
To prove this statement a processing line on pyrolysis of scrap tires was presented. This system has many advantages, which make it environment friendly and economically sound. First of all treatment of scarp tires without formation of secondary wastes was developed. There is no secondary load on the environment.
Energy saving method, which was embodied due to usage of two reactors, allows to consume less energy.
Good sealing of reactors and other processing apparatus provides decreasing air emissions into atmosphere from the system.
Off-line functionate of tire cutter allows to locate it at the source of raw materials. For instance, many landfills presently contain thousands or millions of scrap tires and the apparatus can be located near such landfill so that the tires can be easily acquired for use in the process in the apparatus.
Low sulfur liquid fuel should be marked separately. It was achieved due to limited range of temperature. This maneuver provides cost decrease on additional purification of high sulfur fuel.
Evidently investigation of scrap tires accumulation problem, their management, refer to set of laws and normatives, and also statistical data show that scrap tires recycling is an economically profitable and ecologically effective solution of two actual problems: looking for alternative sources of energy and how to treat accumulated scrap tires. This direction of investigation is rather perspective, and can show all the people how to save our lives and our Earth.

References

1. *Антифеев В.Н.* Моторное топливо транспорта 21 века. Экологические, сырьевые и технические аспекты // Приоритетные направления развития городской науки на период до 2005 г.: материалы науч.-практ. конф. − М.: РУДН, 2001. − С. 17−23.
2. *Платэ Н.А.* Некоторые аспекты создания экологически чистых топлив XXI века // Нефтехимия. − 2001. − Т. 41, № 1. − С. 3−16.
3. *Valerie L. Shulman*. Tire Recycling after 2000: Status and Options // ETRA Publications, 75116. − Paris, France, 2000.
4. *Регенерация* и другие методы переработки старой резины: сб. ст. / под ред. В.Е. Гуля, П.Н. Орловского, И.А. Шохина. − М: Химия, 1966. − 140 с.
5. *Торнер Р.В.* Теоретические основы переработки полимеров. − М.: Химия, 1977. − 236 с.
6. *Створення* комплексу по переробці гумотехнічних відходів, в тому числі автомобільних шин методом каталітичного низькотемпературного піролізу. − Павлоград: ТОВ «РТІ Хімпром», 2006. − 57 с.
7. *Булавин А.В., Пашкевич В.Н.* Переработка автомобильных шин методом низкотемпературного пиролиза. − Л.: Химия, 1999. − 123 с.

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