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Complex processing of rubber waste through energy recovery

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This article deals with the applied energy recovery solutions for complex processing of rubber waste for energy recovery. It deals specifically with the solution that could maximize possible use of all rubber waste and does not create no additional waste that disposal would be expensive and dangerous for the environment. The project is economically viable and energy self-sufficient. The outputs of the process could replace natural gas and crude oil products. The other part of the process is also the separation of metals, which can be returned to the metallurgical secondary production.

***Key words**: Rubber waste, energy recovery, energy utilization of rubber waste, tires, scrap tires, rubber waste recycling, fuel, natural gas.*

Introduction

Constantly increasing production of rubber products such as tires, conveyor belts, cables, gaskets or footwear made of rubber and the associated subsequent accumulation of rubber waste results in an increasing trend for energy recovery using rubber waste as an alternative fuel source. However, there are many difficulties associated with the recycling of this waste [1, 2].

Many authors come with various methods of recycling or degradation of discarded tires and other rubber waste [3]. In the study “Waste type rubber as a secondary fuel and power plants” [4], the use of waste tires in the combustion of coal and the subsequent emission reduction and effective utilization of energy from waste tires are explained. The Article “Waste tire pyrolysis - A review” [5, 6] is dedicated to pyrolysis as an attractive thermochemical process to tackle the waste tire disposal problem while allowing energy recovery. Given this waste-to-energy pathway, a comprehensive review has been carried out in order to show the effects of the main process conditions on the physicochemical properties and distributions of the resulting products. The essential features of an efficient and environmentally attractive pyrolysis for used tires valorisation with energy and material recovery present the article “Features of an efficient and attractive environmentally used tires pyrolysis with energy and material recovery” [7].This article showed that if carefully controlled, tire pyrolysis can produce some valuable products. In the article “Pyrolysis, Combustion, and Steam Gasification of Various Types of Scrap Tires for Energy Recovery” [8], the pyrolysis processes were investigated. The results indicated that the scrap tires can be used as a potential energy resource. The article “Comparative life cycle assessment of beneficial applications for scrap tires” [9] shows that life cycle assessment is used to determine the most environmentally beneficial alternatives for reuse of scrap tires, based on the concept of industrial ecology. Life cycle inventory data are collected from primary industry sources as well as published literature, and life cycle impact analysis is performed using the TRACI tool. The results indicate that beneficial reuse of scrap tires, particularly in cement plants and artificial turf, provides reductions in greenhouse gas (GHG) emissions, air toxics, and water consumption. Rubber is also used to produce certain types of footwear. The next paper is titled “Shoe manufacturing wastes characterization of properties and recovery options” [10]. This paper deals with the characterization of the chemical and physical properties of representative types of shoe manufacturing wastes, the quality profile of a particular material recovery finalized to a soil destination, and the flue gas emissions from burning tests in view of the potential for energy recovery [11].

Our team of authors, in relation to the above study and years of practical and theoretical experience in these issues in cooperation with LTS Ostrava and VÚCHZ Brno, Inc., came with an energy evaluation of rubber material, which would be applicable not only for cement, lime kilns and incinerators, but also for conventional energy production plants operating on the basis of combined production of heat and electricity. They strive for a solution that would be the maximum possible extent of energy using all the rubber waste and will not create

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additional secondary waste and will maximize the use of the energy potential of rubber waste without negative impact on the environment.

Rubber waste can be characterized as a set of products that already had lost its useful properties due to damage, age or redundancy and will become the waste category "O - Other waste". The most famous rubber waste are tires of personal vehicles and trucks. A significant segment of rubber waste is represented by conveyor belts in deep and surface mines, cement works, lime factories, brickworks, etc. It is known, that also another waste that is rubber based exists like rubber - metal waste from industry, rubber cables, rubber seals of automobiles, rubber profiles and more (Fig. 1). Figure 1 shows a block diagram of the rubber waste and its mechanical pre-treatment. Inputs are on the left side of the image. These inputs are inserted into the mechanical separation process. Subsequently, the rubber that can't be mechanically processed goes into the thermal separation (pyrolysis). The outputs of the process are shown in yellow (metals and feedstock for pyrolysis).

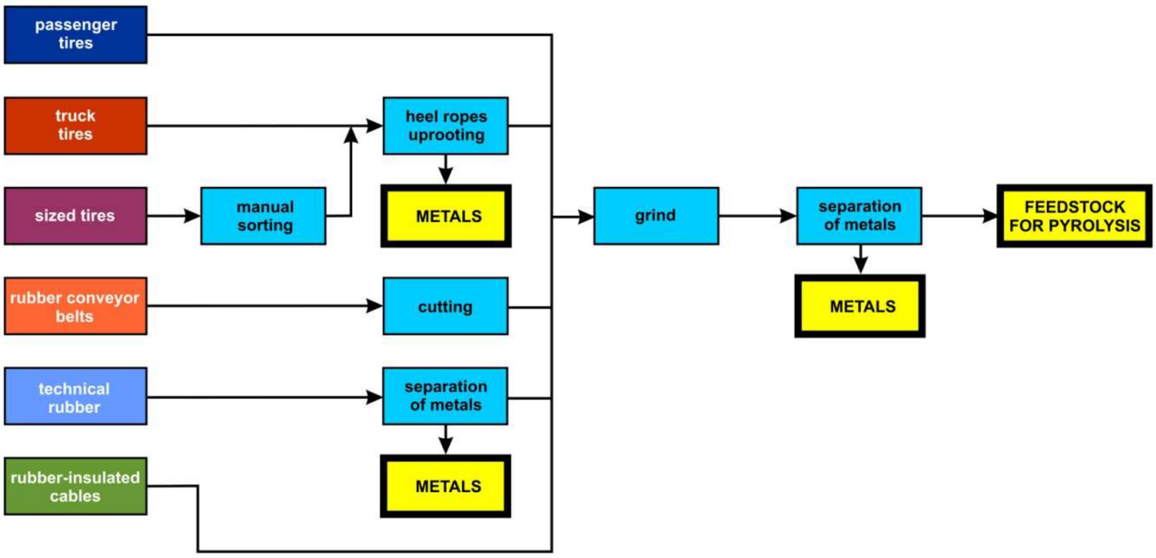

Fig. 1. Block diagram of rubber waste and its mechanical pre-treatment.

Rubber waste is currently used for energy in specialized incinerators and furnaces of cement clinker. Used tires can be also used for energy gain, instead of founding a tire landfill. Due to the completion of the process of landfilling of waste in 2024, the share of such saved tires will be no longer significant. Part of worn tires are also used to make surfaces for sports and special insulation covering. Experts are also trying to add tire debris into bituminous mixes for road constructions. Because the rise of rubber based waste of used tires in the Czech Republic is about 60 thousand tons a year, their current energy utilization in specialized incinerators is negligible. Rubber waste due to its specific chemical composition represents a very significant energy potential, which with the use of conventional energy boilers should bring substantial savings of fossil fuels. The problem, which prevents the expansion of the energy use of rubber waste as fuel, is legislative need of transforming waste into fuel and proper technological equipment that would use rubber-based fuel for the production of thermal energy **without adverse effects on the environment.**

During the last ten years, the projects that deal with the conversion of used tires into fuel or raw materials also useful in the chemical industry have appeared. Mostly, it is a technology of thermal decomposition of rubber to hydrocarbons and solid carbon residue. Despite some advances in technology, these projects are not yet commercial due to frequent failure rate, unresolved legal issues and the resistance of general public, municipalities, and environmental activists, who see an analogy of incinerators in the technology of thermal decomposition.

Methods- suggested solution

Our research team is engaged in a solution that would be able to maximize the possible energy of all rubber waste. This solution must be comprehensive and must not create additional, especially hazardous secondary waste. Emissions from waste incineration must not exceed emissions from boilers to natural gas, according to the methodology of the Ministry of Environment. There are two possible ways of processing of the rubber waste. The first method is the evaluation of the material (Fig. 2), and the other option is called the energy recovery (Fig. 3).

Because rubber is produced on the basis of polymerization or copolymerization of unsaturated hydrocarbons (polybutadiene, the copolymer butadiene - styrene and ethylene - propylene rubbers), an occasion of its reverse transformation process of depolymerization on usable fuel for energy production exists. The most desirable secondary raw materials are liquid hydrocarbons, which are divided into a light fraction with refinery process (gasoline) boiling up to 80 ° C, intermediate fractions (naphtha and gas oil) boiling in the range of 80-170 °C and a heavy fraction (oil and heavy oil) boiling in the temperature interval of 170-340 °C. In the case of energy recovery of liquid hydrocarbons on the basis of co-firing with other products of depolymerization, the refining process is not required and investment costs of complex technology would be inappropriately increased. Many of rubber waste contain a proportion of sulfur and sulfur compounds, which were used in the manufacture of originating products as plasticizers. As the most common example of this case is the tire for winter use, which comprise about 3 % sulfur.

Sulfur content in the exhaust products of depolymerization must be minimized to a level permissible under applicable standards. The solution is to transform the sulfur compounds to hydrogen sulfide (H_2S) and the application of the Claus process for the production of elemental sulfur. This is a capital intensive but perfectly mastered technology that does not produce waste, and it is a very effective process. Pure elemental sulfur is also applicable to the market of chemical raw materials. The chemically comparable product is produced in refineries and coking plants.

During the process of depolymerization, hydrocarbon gasses that don't condense at normal temperature also occur. It is a mixture of purified gas with a high energy potential (about 42 MJ / m^3), which can be used in the heating process of depolymerization itself as well as for generating electricity by cogeneration for crushers, conveyors, and other energy-consuming appliance. The surplus of electrical energy can be transformed to the required voltage supplied to the distribution network. According to local conditions of the project, the accumulation of gas in high-pressure vessels and its distribution as in the case of liquefied gasses based on propane, propane-butane, and isobutane are also viable. The last product of depolymerization of rubber waste is called solid residue, which is made up of tiny carbon with the enlarged surface, soot, tiny steel cords and debris of inorganic origin. This dirt with changing composition prevents from more significant energy use of solid residue from the process of depolymerization from a legislative point of view, although quantitative and qualitative terms differ just a little from impurities in the fuel coke.

With a suitable method of processing (magnetic separation and flotation), a pure carbon for the chemical industry can be obtained, or a solid residue can be used after mechanical treatment (magnetic separation, crushing and grinding) as a fuel with high calorific value (about 28 to 32 MJ / kg) for fluidized bed boilers. By applying suitable flotation reagents, inorganic contaminants can be removed from the solid residue including heavy metals. The added value of such fuel will grow in the market to 6000 - 7000, - CZK / ton. The price of our fuel was compared with the price of fuel coke. Except depolymerization, there is a possibility to obtain significant amounts of metals from rubber waste. These metals occur in the pre-treatment of raw material before the process of depolymerization (tire beads), and they are also contained in the solid residue after the process of depolymerization. All contained metals are not degraded by oxidation as in incinerators and can be utilized in the market of secondary raw materials for the steel industry. This process is shown in Figure 2.

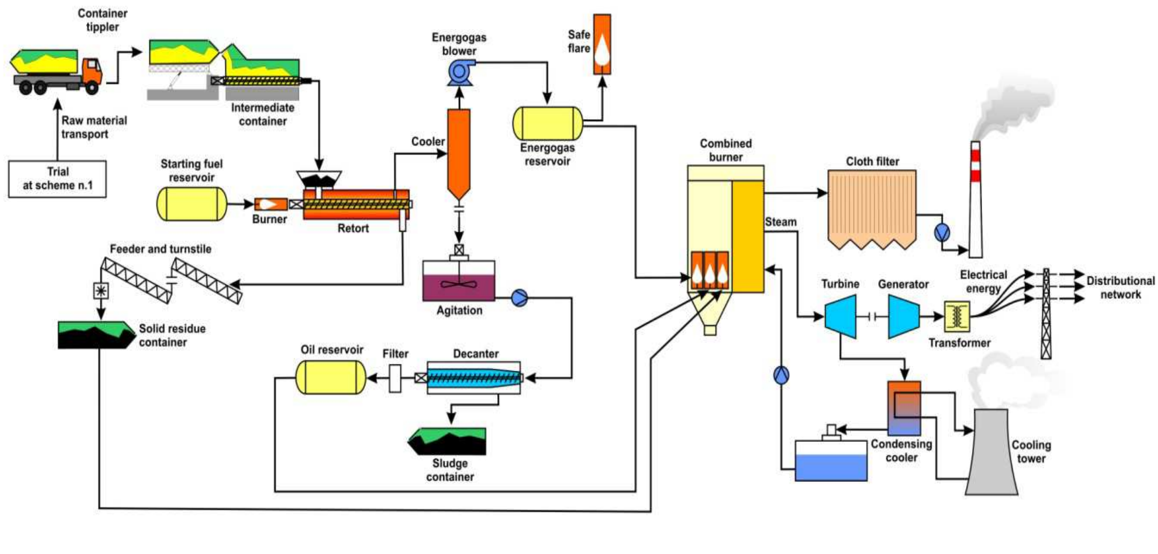

Fig. 2. Scheme of processing of rubber waste for the production of fuel applicable to conventional power plants without fluidized bed combustion.

Chemical analysis of the pyrolysis products

This chapter lists the various chemical analysis of the input material - rubber waste, chemical analysis of pyrolysis coke, pyrolysis oil, and pyrolysis gas. In cooperation between LTS Ostrava and chemical laboratory VUCHZ in Brno, a series of chemical analyzes were realized. For the following article, data were separated and described in the following tables. The next chapter presents the chemical analyzes of individual pyrolysis products. We want to prove that the composition of pyrolysis products does not negatively affect the environment. That is why it is necessary to do a chemical analysis.

Tab. 1. Elemental analysis of input material.

Material	The individual components of the material [%]								
	C	H_2	N_2	S	O_2	M	FC	V	A
Waste rubber	85,4	7,57	0,48	0,44	0,01	0,98	23,03	70,86	6,11

Tab. 2. The chemical analysis of the pyrolysis coke.

Analytical indicator	unit of measure	protocol amount	Analytical indicator	unit of measure	protocol amount
Total water	% (m/m)	0,95	Content of heavy metals in ashes:		
Ash in the anhydrous state	%(m/m)	9,45	Arsenic, As	%(m/m)	< 0,001
Calorific value in original condition	KJ/kg	34 814	Cadmium, Cd	%(m/m)	0,001
Sulfur in the anhydrous state	%(m/m)	1,61	Chrome, Cr	%(m/m)	0,001
Nitrogen in the anhydrous state	%(m/m)	0,29	Copper, Cu	%(m/m)	0,006
Chlorine in the anhydrous state	%(m/m)	0,034	Mercury, Hg	%(m/m)	<0,001
Sum of PCB	mg/kg	<0,05	Lead, Pb	%(m/m)	0,013
			Zinc, Zn	%(m/m)	9,71

The sum of PCB is less than 0,05 – which is the limit. Chlorine is also allowed at the rate of 0,05; our rate is 0,034. The measured quantities of heavy metals such as cadmium, chrome, copper, mercury and lead are smaller than allowed, see Table 2.

Tab. 3. The chemical analysis of the pyrolysis oil.

Analytical indicator	unit of measure	protocol amount	Analytical indicator	unit of measure	protocol amount
Water content	% (m/m)	12	Content of heavy metals in ashes:		
Ash content	%(m/m)	0,005	Arsenic, As	mg/kg of dry matter	<40
Calorific value	KJ/kg	40 990	Cadmium, Cd	mg/kg of dry matter	<0,25
Sulphur content	%(m/m)	1,05	Chrome, Cr	mg/kg of dry matter	<1,5
Nitrogen content	%(m/m)	0,85	Copper, Cu	mg/kg of dry matter	<0,25
Total chlorine	%(m/m)	0,025	Lead, Pb	mg/kg of dry matter	<2,5
Sum of PCB	mg/kg suš.	1,076	Zinc, Zn	mg/kg of dry matter	3,08
Density at 40 ° C	g/cm³	0,9	Mercury, Hg	mg/kg of dry matter	0,0197
Kinematic viscosity at 40 ° C	mm²/s	5,3			
Flash point at o.k.	°C	82			

In Table 4, we compare a natural gas with a pyrolysis gas produced by us, with properties of the pyrolysis gas produced at the process temperature of 650 °C, and the transit of natural gas.. The calorific value showed that pyrolysis gas can replace natural gas.

Pyrolytic decomposition of the rubber waste was conducted on technology PYROMATIC 50. Individual fractions were formed at the process temperature of 650 °C. The results of measurements prove that physicochemical modifications of individual fractions are applicable when using ordinary refinery and processing technologies [13, 14].

Our products do not have a negative impact on the environment because chemical analysis showed that it does not exceed the permitted substances in emissions.

Tab. 4. The chemical analysis of the pyrolysis gas.

Name	Marking	Unit	Pyrol. gas (pneu)	Natural Gas
Calorific value	Q_i	$[MJ.m^{-3}_{N}]$	31,79	35,87
Combustion heat	Q_s	$[MJ.m^{-3}_{N}]$	34,68	39,79
Density	ρ	$[kg.m^{-3}_{N}]$	1,04	0,73
Relative density	d	[1]	0,8	0,56
Specific heat capacity	c_p	$[kJ.m^{-3}_{N}.K^{-1}]$	1,33	1,56
Vol. the proportion of clean combustibles	$\Omega_{\check{C}H}$	[%]	63,7	99,09
Vol. the proportion of CO in the pure combustible	Ω_{CO}	[%]	4,55	0
The volume fraction of H2 in pure combustible	Ω_{H2}	[%]	44,43	0
The volume fraction of CH4 in pure combustible	Ω_{CH4}	[%]	7,22	99,29
Volume fraction of pure C2H4 in pure combustible	Ω_{C2H4}	[%]	8,16	0
Volume fraction of pure C2H6 in pure combustible	Ω_{C2H6}	[%]	9,89	0,44
ΣC3HY volume fraction in pure combustible	$\Omega_{\sum C3HY}$	[%]	10,99	0
ΣC4HY volume fraction in pure combustible	$\Omega_{\sum C4HY}$	[%]	7,54	0,16
ΣC5HY volume fraction in pure combustible	$\Omega_{\sum C5HY}$	[%]	5,02	0,07
ΣC6HY volume fraction in pure combustible	$\Omega_{\sum C6HY}$	[%]	2,2	0,03

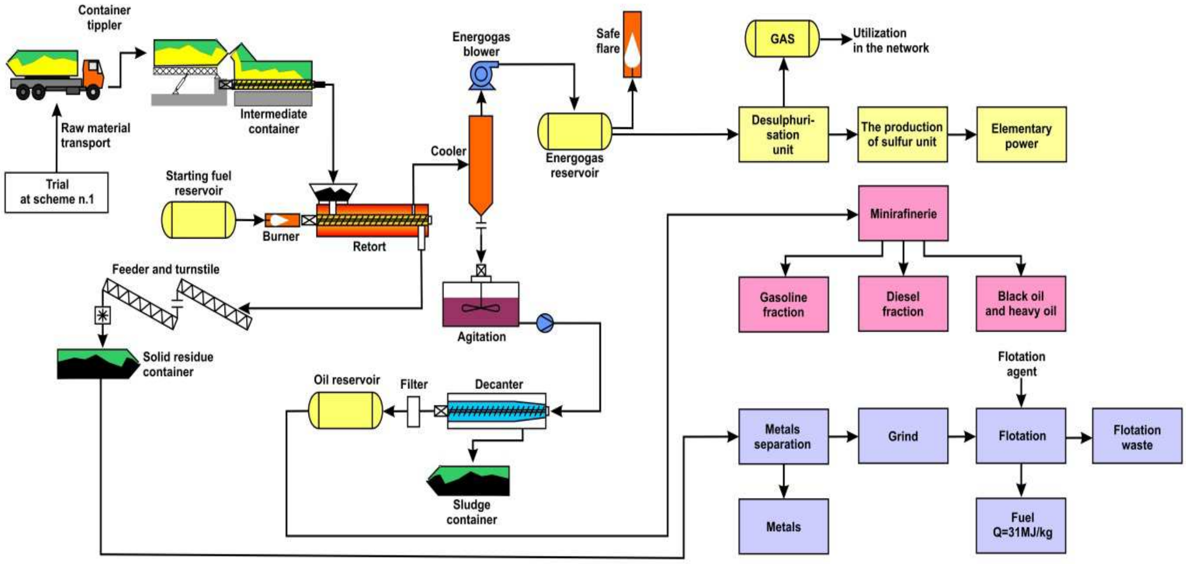

Fig. 3. Energy evaluation of rubber waste at the plant with fluidized bed combustion.

The second solution of the energy use of rubber waste (Fig. 3), especially of used tires, involves connection of depolymerization technology with the physicochemical processing of products and fluidized bed boiler, which burns down all products of depolymerization. The process of transformation from waste into fuel comes up after physicochemical processing of depolymerization products. The incineration of gaseous and liquid hydrocarbons is carried out in the specialized mixed burner. The solid carbonaceous residue of the depolymerization process is fed directly into the fluidized bed. Selection of performance and parameters of the fluid is dependent on the boiler type and the desired efficiency of the steam turbine. Depolymerization lines can be modularly connected with the physicochemical processing plant, which brings savings in investment costs.

Results

Impacts of solution

The impacts of a solution for this project are not geographically restricted. The results of the project can be applied not only within the European Union, but also outside the European Union. Especially in developing countries, the solution of collecting and disposal of rubber waste is not developed at all. The use of secondary raw materials based on liquid hydrocarbons should be economically very useful for countries without oil and other fossil fuels. Illegal dumps of tires in the countries of the former Soviet Union and in developing countries in Africa and Asia contain hundreds of tons of valuable waste. Its destruction is not yet lucrative for the local authorities and businesses.

The energy potential of some secondary products of depolymerization and their material value should be interesting for the economy of some countries outside Europe.

Environmental benefits

The process of complex processing of rubber waste through material and energy recovery in the specific conditions of the country has a very significant environmental benefit. It is an energetically interesting material, and its process is very friendly to the environment (see previous chapter „chemical analysis“). The technology is not harmful to the atmosphere. In the context of the water protection, more-casing containers known from the using of liquid fuels can be easily applied.

Generally speaking, voluntary and economic motivation can lead to reaching its goal sooner than the commands, prohibitions and persecution by the government and local authorities. For this reason, it would be good to encourage the population to purchase tires and other rubber waste, especially in developing countries. Illegal dumps would have been transformed into technological lines for complex dealing with rubber waste.

Economic benefits

According to Fig. 1, we can conclude that we can get metals, liquid hydrocarbons, carbon and elemental sulfur from rubber waste, Fig. 2. Application of our product - pyrolysis gas is comparable with natural gas, so it can be replaced, and elemental sulfur is also marketable. Liquid hydrocarbons, such as gasoline fraction, diesel fraction, fuel oil and heavy oil are also marketable as the input raw material for the petrochemical industry (raw fuel). The quality fuel is created after adding additives to it.

In the context of the entire technology, there is a complex process of separation of metals, where bigger elements can be separated mechanically, and smaller elements must be separated thermally. The separated metals can be sold again as a secondary raw material.

Another product is pure carbon, which can be used as feedstock for producing activated carbon that is used in wastewater treatment plants, in filters, cooker hoods, etc.).

Three separate economic variables are available in case of the economic contribution:

- The proceeds from the sale of secondary raw materials (metals, liquid hydrocarbons, carbon, and sulfur).
- The proceeds from the sale of electricity and heat.
- Savings of the fossil fuels and an increase of energy self-sufficiency of the country.

According to the territorial localization of technological lines, revenues will naturally vary.

Effect on Employment

Lines for complex processing of rubber waste can create new job opportunities in the labor market. For the operation, line workers are needed for handling tankers, loaders and other blue-collar jobs with minimum requirements on education. Due to the continuous use of this technology all four shifts will be needed to fill with workers.

The secondary benefits of the project

As secondary benefits of the project can be highlighted following: The composition of raw materials that arise from rubber waste is similar to the products of primary oil refining. For this reason, crude oil can be replaced with these raw materials. Worldwide, there was a move away from large central power plants to a large number of smaller plants (Blackout). Our project is supporting a global policy based on small and medium sources. Regarding the territorial dimension, for example, Portugal has not fossil fuel resources. The price of energy will then be equal to the price of fuel plus shipping. Greece and Cyprus also import fuel. Therefore, rubber waste is a good alternative power source. In this case, the population can be positively motivated to buy rubber waste, which could lead to the end of so-called illegal dumps. Companies that deal with the purchase of such material could better plan their economic results. This application is an analogy to the waste plastics, which have different process requirements, but it is the same process that is already tested.

- Reducing dependence on imports of oil-based raw materials and their products
- Energetics solution for small and medium level
- Use of alternative energy sources
- Change the population attitudes to waste in developing countries
- Solving energy self-sufficiency in isolated areas
- Sustainable development of manufacturing companies
- The application of this process for other types of waste.

Conclusion

The aim of the research team was to demonstrate that adaptation for incineration of waste-based fuel in a conventional power plant is possible. They have succeeded to prove experimentally that the rubber waste may not be burned in special power plants only. The article shows the possible and technically feasible process of transforming waste into a product without any unwanted secondary waste. This procedure is legislatively correct, and it is recommended by the European Union.

We succeeded to verify experimentally the process of material assessment and energy recovery of rubber waste. The advantage of one or another process depends on specific conditions in the country. For example, electrical energy from tires is not subsidized in the Czech Republic but it is subsidized in Slovakia. In Poland, there is a high demand for liquid hydrocarbons. Another positive aspect of this process is that third world countries do not have electrical power. In each geographic area, one of these processes (Fig. 2 and 3) may be applied according to local conditions [12].

It has been proven that this is a good direction for research on possibilities of energy utilization and material evaluation of other kinds of waste like mixed plastics and residues from beverage cartons. In the future, we can focus on the decontamination and subsequent recovery of hazardous waste.

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