

SCRAP TYRES AND EXPLOITATION OPTIONS FOR TYRE RUBBER MIX

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This paper deals with scrap tyre management and current exploitation routes. The disposal of tyre waste is increasing day by day at exponential rate. Exploitation of end-of-life tyres is a significant environmental issue and challenge for all countries. Rubber has long-term decay in natural conditions due to high durability for lot of climate or soil exposure and biological attacks. Scrap tyres within most countries are burned up nowadays, but this has generally negative influence. From an economic standpoint, however, the profit derived from energy recovery by tyre incineration would be offset by the expense of meeting pollution legislation. Scrap tyres can be utilized in various rubber applications. Recommended solution is to thermally reprocess tyre waste into valuable products. One of thermal processes is pyrolysis that tyre waste can be converted into crude gas, oil and solid products. For instance, solid product can be used as carbon black with quality improvements.

KEYWORDS

scrap tyres, secondary raw material, thermal treatment

1 INTRODUCTION

Waste or end-of-life tyres fall under the general solid waste category give rise to land filling, health and environmental challenges. As a result, majority of these waste tyres accumulate in large quantities at landfill sites or end up being illegally disposed in open fields. The history of waste tyres to energy (WTE) is a long story of learning, experimenting and evolution. Scrap tyres have been used for energy within Japan, Europe, and the United States since the 1970s. Paper manufacturing mills began exploiting tyre-derived fuel (TDF) in the United States within the late 1970s. The experience base has broadened significantly during the last 15 to 20 years as tyres have become recognized as a viable alternative fuel in appropriate combustion processes. Once a tyre is in a scrap tyre pile, its uses are limited but it is still a viable option for energy exploitation. Applications include cement kilns, industrial boilers, utilities, and dedicated electrical generation facilities, etc. The partially burnt TDF in turn contributes to more environmental pollution. There have been efforts not only to overcome this but also to find value addition to these scrap rubber wastes exploiting them as secondary resource of raw materials. A better solution from an environmental and economic stand-point is to thermally reprocess scrap rubber into valuable

products such as activated carbon, or other solid carbon forms, e.g. carbon black, graphite, carbon fibres, etc.

The following sections discuss the energy and chemical characteristics of tyres, as well as long-term experience in major energy applications. The sections within this paper tell this story from many different points of view. Engineers have been working on the recovery of the energy in wastes from the time that steam engines for power and heat generation were first in operation within the late 1800s.

Energy provide and waste management are great challenges that humans have faced for millennia. Tremendous progress has occurred, yet these issues are still important today. To meet these challenges we must move to an atom economy where every atom is exploited in the best possible manner. To achieve this goal, a fundamental understanding of the underlying mechanisms and processes of energy and waste generation is necessary.

One of the main challenges of modern society is the rising rate of solid waste generated by man's activities which has poised a major environmental concern. The disposal of scrap tyres and other polyisoprene based products is a large fraction of such problems as 178731 tyres are estimated to reach their end of life cycle annually within Slovakia. They are not biologically degradable and leading to problems with their disposal. Over the years landfill and open dumping (stock piling) were the common ways in handling the problem of tyres put out of service. However, landfills take up valuable land space due to the bulky nature of tyres which cannot be compacted neither does it degrade easily. Dumped waste tyres in massive stock piles do not only occupy a large land space but also serve as a potential health and environmental hazard due to the possibility of a fire outbreak with high emissions of toxic gases and as a breeding ground for disease carrying vectors.

No matter how many ways people find to make use of waste tyres, old tyre dumps still spring up around the world. Despite the effort to try making car tyres less harmful to our environment, there is a huge negative impact made throughout the life cycle of the tyre.

2 END-OF-LIFE TYRES AS RAW MATERIAL FOR VALUABLE FUELS - ENERGY OR CHEMICALS

Tyres are designed to be tough and hard-wearing, once they reach their end of life they are difficult to dispose. The main component of tyres, rubber, is a chemically cross-linked polymer; which is neither fusible nor soluble, consequently cannot be remoulded without degradation [Anonym 2012]. In rubber manufacturing, vulcanisation thermally disintegrates rubber creating a hard plastic rubber that retains its form for tyre application. Antioxidants are added into tyres to counter zone effects and material fatigue. The addition of steel, rayon and nylon plus the process of vulcanisation contribute to the non-recycling character of tyres. The processes and facilities required to extract rubber, steel and fibres from tyres are costly, and the resultant products are generally of low value [Adhikari 2000]. Two major approaches to address this problem are recycling and the reclaiming of raw rubber materials or selected chemicals.

2.1 What do Tyres Consist of?

Characteristics and composition of scrap tyres. Tyres are made up of different types of rubber elastomers (natural or synthetic rubber) with varying composition, carbon black, stabilizers, antioxidants, sulphur, hydrocarbon oils, zinc oxides, textile or steel cords [Undri 2014, Williams 2013, Islam 2008, Williams 1995], and so forth.

An average car tyre weighs around 8 kg new and loses around 1.5 kg with wear during use. Tyres comprise between 80 and 85 % rubber compound by weight, with the remainder made up of steel, fabric and cording. The rubber compound only consists of about 56 % rubber by weight, the rest comprising fine carbon powder known as carbon black (30 %), oil (10 %) zinc oxide (2 %) sulphur (2 %) and other chemicals such as vulcanisation activators, processing aids, silica and inorganic fillers (1 %). The rubber component is a mix of natural and synthetic polymers, the latter usually styrene butadiene or SBR. The precise ratio depends on the manufacturer, with lorry tyres generally richer in natural rubber than car tyres which commonly only comprise 25 % natural rubber. During manufacture, the rubber compound is vulcanised using a high temperature process which results in strong bonding at a molecular level between the various components. This makes it difficult to separate them without using high temperatures and/or elaborate chemical procedures. Only a small amount of rubber from waste tyres – typically up to 2 % - can be normally used in the manufacture of new tyres.

Processing waste into alternative fuels, used directly or in order to produce electricity and heat is becoming increasingly preferred way to use energy characteristics of those wastes, properly in the WtL processes of (Waste to Liquid) or WtE (Waste to Energy).

The complex morphology and unstable composition of the waste substances, as well as formal and legal requirements are the main cause of relatively small use of waste (including scrap tyres) within the energy sector, particularly in the countries of Central and Eastern Europe. The legal requirements in many European countries allowed energy recovery, if it meets the emissions, environmental, technological and social requirements.

List of industrial plants, that can currently use alternative fuels, is contained in the relevant legislation, which gives the possibility of using these fuels in existing systems.

There are following types listed:

- cement kilns
- lime kilns
- blast furnaces
- coke oven batteries
- rotary kilns for ores burning
- power and industrial boilers.

Under current law, alternative fuels can be used in combustion or co-incineration processes at waste incineration plants. Regulations dealing with alternative fuels clearly stated limits for LHV and emissions for the relevant processes. Depending on whether the fuel will be used as the only material or undergo the co-incineration process, they must comply with the standards specified for a given emission. It should be remembered, that the emission standards for co-firing installations are slightly lower than for combustion plants, and therefore meeting the threshold may be associated with some modernization and technological

investments. Co-incineration of non-hazardous waste in quantities of less than 1 % of the combusted fuel weight means not applying to such process the emission standards just like for co-firing process, but only emission standards, such as for energy fuel combustion. In addition, co-firing will cause the need to change the status of the power plant, and it will change the status of waste products (fly ash and slag). These products have different code marks and foremost it subjects to other development opportunities. The application of fly ash within construction is limited by standard PN-EN 450:2006 for the waste from the coal combustion. The use of such waste is also related to the possession of relevant authorizations (residues from the combustion of used tyres have e.g. heavy metals).

Index of modern methods of waste tyres management is shown in following Tab. 1.

Type	Process	Products
I - Physical	Re-treading	New tyres
	Re-use	Barriers, covers
	Use for engineering	Landfill engineering, or for various applications including dock fenders, artificial reefs and barriers, playground swings, etc.
	Granulation	Asphalt additives, re-use in other products such as a layer under-lining, playground and track surfaces;
II - Thermal	De-vulcanisation	For producing de-vulcanised rubber from waste tyres
	Co-incineration in cement kilns and power boilers	Replacement of fossil fuels, energy
	Special combustion	Energy and steel for reuse
	Pyrolysis	Carbon black, pyrolysis oil and synthetic gas – syngas;
	Pyrolysis + gasification	Carbon black, steel and synthetic gas; the low value of the end products, which are usually fuels (oil, pyrolysis gas, char, etc.)
	Gasification	Steel, synthesis gas
	Cryogenics	Steel, rubbery granulate
	Microwave method	This process can produce products similar to virgin rubber
III - Nanophase	Thermal plasma	Production of nanophase materials is by using an ultrafine powder as the starting material. Preliminary experiments produced particles with diameters in the range 5 - 100 nm. Bulk production of nanoparticles or nano-powders.

Table 1. Methods of waste tyres management [Heermann 2001]

Installations for the recovery or disposal of non-hazardous waste by using thermal processes have to be considered for installations that may significantly affect the environment. Technical requirements for such systems are also well defined in the relevant legislation. Emission standards for co-incineration plants are related to such pollutants as:

- Dust
- Total organic carbon
- Hydrogen chloride
- Hydrogen fluoride
- Sulphur dioxide
- Nitrogen oxide and nitrogen dioxide
- Carbon monoxide.

Measurements of these emissions should be carried out continuously. In addition, concentrations of dioxins, furans and heavy metals listed in the Regulations should be periodically measured.

2.2 Options for Tyre Recovery

- 1 Re-treading
- 2 Re-use
- 3 Use for engineering
- 4 Granulation to produce rubber crumb
- 5 De-Vulcanisation
- 6 Incineration
- 7 Combustion or burning
- 8 Pyrolysis
- 9 Gasification
- 10 Cryogenics
- 11 Microwave method
- 12 Thermal plasma and nanomaterials.

2.2.1 Re-treading

Re-tread also referred to as “remould” involves buffing away of the remaining tread in a spent tyre and replacing it with a new tread rubber strip by vulcanization. It is carried out only on used tyres casing that have been inspected and repaired. Although it is economically advantageous, product quality confidence is a major challenge of the process.

Manufacturing a re-tread for an average car saves around 75 % of the energy used to make a new tyre, equivalent to around 4.5 gallons of oil. The saving increases to the equivalent of around 15 gallons of oil on average in the case of lorry tyres.

Collected tyres for re-treading are first inspected and if found suitable the old tread is mechanically removed by a process called buffing. This produces rubber granulate which can be used for other products. The new tread is applied using one of two processes. In the pre-cure process the tread rubber has already been vulcanised with the new tread prior to application. In the mould-cure process unvulcanised rubber is applied to the buffed tyre before the tread is vulcanised onto it.

2.2.2 Re-use

Around 16 % of tyres had sufficient tread as to be suitable for reuse without further treatment. The regulations state that tyres should have a minimum tread depth of 2 mm across the entire breadth of the tyre and should be clearly marked as part-worn at the point of sale.

2.2.3 Use for Engineering

Around 4 % of waste tyres were used for landfill engineering. These are usually used whole to line the base of new landfill sites to provide for drainage. Around 5 % of used tyres were also used for various applications including dock fenders, artificial reefs and barriers and playground swings. New engineering uses include the community buildings and houses which have recently been constructed using whole tyres in the walls.

2.2.4 Mechanical or cryogenic method, to produce rubber crumb

Both mechanical and cryogenic (grinding of waste tyres at temperatures of $-80\text{ }^{\circ}\text{C}$ to $-100\text{ }^{\circ}\text{C}$ using liquid nitrogen) recycling of used tyres involve the milling of tyres to produce ground rubber of different particle sizes. The fine ground rubber can be used in varieties of application such as an additive in road asphalt, sports and children playground surfacing, carpets, and other rubber products. However, the limited market for the product and a high cost of running the process are disadvantages.

Rubber crumb is the main source of material for items produced from waste tyres. Around 22 % of waste tyres were recycled, mostly in the form of rubber crumb. The term “crumb” is generally used to describe any rubber compound which has been reduced to a powder but in this context it refers to the granular material produced from waste tyres which ranges in size from a few millimetres to a few thousands of a millimetre. There are three main types:

Buffed crumb is produced from part-worn tyres submitted for re-treading. This is free of fabric or steel and comprises a high quality, abrasion-resistant rubber compound. This was the traditional resource of crumb in the UK until direct crumbing started to increase in the last few years.

Whole tyre crumb is produced at room temperature directly from scrap tyres. These are first shredded to about 3-5 cm in size then passed through a coarse mill then through finer mills and screens. The shredding of steel-containing tyres, now almost universal, is energy intensive with rapid wear and tear of equipment. Zero-waste systems have been developed which make use of all the waste steel and other components. The cost of the operation increases dramatically the finer the crumb required. The equipment itself is very expensive – ranging from €100,000 to €1.25 million – and its operation poses many health and safety considerations. New water-jet crumbing equipment is cleaner, cheaper and easier to operate but prices for this are expected to be higher. A further advantage of the water-jet equipment is that any size crumb can be produced down to the finest powder with a single process and it may be possible to fabricate small items such as washers directly.

Rubber crumb and de-vulcanised rubber can be combined with various thermoplastic materials to produce reduced cost materials without sacrificing critical properties or processing characteristics. The rubber can be used to modify Linear Low Density Polyethylene (LLDPE), Polypropylene (PP), Polyurethane (PU) and Polyvinylchloride (PVC) among others. The rubber particles are blended at levels of around 5-70 %. Another use for rubber crumb and shredded tyres is as mulch and compost. The crumb confers good drainage qualities and the shredded rubber looks very similar to mulch produced from bark.

2.2.5 De-vulcanisation

A number of experimental processes are being investigated for producing de-vulcanised rubber from tyres in which the sulphur links are broken, enabling the rubber to be reprocessed and cured like virgin rubber compound. These include ultrasonic and microwave techniques. If shown to be economically viable, these could greatly increase the potential for tyre recycling.

2.2.6 Incineration

The incineration of scrap tyres may be defined as the reduction of combustible wastes to inert residue by controlled high-temperature combustion. The combustion process is spontaneous above 400 °C. It is a highly exothermic process and once the process has stabilized it becomes self-supporting. The thermal efficiency of this process is approximately 40 % [Fortuna 1997]. Waste tyres having a calorific value of 7.5 - 8 MJ.kg⁻¹, are used as fuel in incinerators. The gas produced may be used as heat for industrial processing or electricity production. Burning of refuse in steam-generating incinerators and using it as a supplementary fuel is advanced and proven waste to energy utilisation [Anonym 2006]. Furnace design and efficiency influences the general combustion performance. Incinerators have to be designed for excellent burning and reduced soot production. Walls and furnace beds must be able to withstand high temperatures of approximately 1150 °C. Combustion efficiency, the ratio of thermal energy output to global energy input, usually depends on interdependent factors such as the fuel's physical characteristics, plant design, manufacturing and operating conditions. Incineration produces high levels of energy recovery as tyre rubber has a calorific greater than top-grade coal (32.5 MJ.kg⁻¹ compared to 29 MJ.kg⁻¹ for coal). The tyres are normally shredded first to produce so-called tyre-derived fuel, known as TDF. They replace around 25 % of the coal which would otherwise be used. Around 8 % of waste tyres were exploited for energy recovery. However, there are a number of environmental concerns surrounding incineration.

2.2.7 Combustion or burning

TDF was the first market for scrap tyres in USA. Whole scrap tyres were used as feedstock for ground rubber and processed tyres were used in civil engineering applications. Based on over 15 years of experience with more than 80 individual facilities, the EPA recognizes that the use of TDF is a viable alternative to the use of fossil fuels. There are several benefits to exploiting tyres as fuel:

- Exploit of TDF reduces the amount of fossil fuels that would otherwise be consumed.
- TDF is less expensive than fossil fuels.
- Diversion of tyres from landfills reserves landfill capacity for other municipal waste and helps prevent scrap tyre piles. Scrap tyre piles pose risks because they provide habitat for disease vectors (such as mosquitoes and rodents), and because they can catch fire, creating large amounts of toxic smoke and hazardous liquids that can contaminate air, water and soils.
- Some state agencies suggest that cement kilns add TDF to their coal fuel in order to decrease emissions of oxides of nitrogen (NOx).

- TDF offers the potential advantage of decreasing emissions of oxides of sulphur (SOx) when used to replace high sulphur coal in cement kiln applications.
- In cement kiln applications, the ash resulting from TDF and coal combustion becomes an integral component of the product, eliminating the landfilling of ash.

The following statement is from an EPA research paper on use of TDF:

TDF can be used successfully as a 10-20 % supplementary fuel in properly designed fuel combustors with good combustion control and add-on particulate controls, such as electrostatic precipitators, or fabric filters. Furthermore, a dedicated tyre-to-energy facility specifically designed to burn TDF as its only fuel has been demonstrated to achieve emission rates much lower than most solid fuel combustors. No field data were available for well-designed combustors with no add-on particulate controls. Laboratory testing of a Rotary Kiln Incinerator Simulator (RKIS) indicated that efficient combustion of supplementary TDF could destroy many volatile and semi volatile air contaminants. However, it is not likely that a solid fuel combustor without add-on particulate controls could satisfy air emission regulatory requirements in the US.

Although scrap tyres can be used as a resource of fuel in cement kilns by combustion method, it is not economically wise and environmentally friendly [Undri 2014, Bianchi 2014, Quek 2013].

2.2.8 Pyrolysis

Pyrolysis is defined as thermal decomposition in an inert atmosphere. Depending on the conditions used, tyres can be pyrolysis to produce a wide range of gaseous and liquid hydrocarbon mixtures together with varying amounts of char. There have been numerous attempts worldwide to produce economically viable techniques for tyre pyrolysis over the last 25 years but commercial-scale plants have tended to fail because of the low value of the end products in relation to capital and operational costs. However, development continues in many countries.

Pyrolysis mainly involves the thermal degradation of tyre rubber at high temperatures (250–900 °C) in oxygen absent environment. It can be performed under vacuum or atmospheric pressure [Jahirul 2012, Beecham 2008]. Amongst other methods such as combustion and gasification used to extract energy from biomass, pyrolysis has received more attention in the area of research because the process conditions can be optimized to produce high energy density liquids, char, and gas. Also, the condensable fraction (bio crude) can be stored and easily transported to where it can be most proficiently utilized. Tyre pyrolysis can be said to be made up of three stages, that is, the release of volatile and moisture at lower temperature succeeded by the thermal decomposition of natural rubber (NR) and the decomposition of polybutadiene (BR) and polybutadiene-styrene rubber at higher temperature, respectively [Anonym 1996, Undri 2014].

The process conditions that can influence the percentage weight of each fraction of pyrolysis include pressure, heating rate, temperature, feed particle sizes, catalysis,

flow rate of inert carrier gas, configuration of reactor used [Martínez 2014], and so forth.

2.2.9 Gasification

Gasification is a sub-stoichiometric oxidation of organic material. The thermochemical process for gasification is more reactive than pyrolysis. It involves the use of air, oxygen (O₂), hydrogen (H₂), or steam/water as a reaction agent. While gasification processes vary considerably, typical gasifiers operate at temperatures between 700 and 800 °C. The energy efficiency of the gasification process is reported to be around 76 % [Manuel 1997]. Most part of the literature data on the waste tyre gasification are collected in fluidized bed reactors and using air as oxidizing agent, while data concerning other experimental designs are hardly found.

2.2.10 Cryogenics or cryomechanical milling process

In the mid-1960s, the technique of grinding scrap rubber, particularly tyres, in cryo-mechanical process was developed [Zanetti 2004]. Cryogenically ground rubber is used in tyres; hoses; belts and mechanical goods; wire and cables and various other applications. This is particularly useful in tyre inner liners. In this process, the rubber is cooled using liquid nitrogen at a temperature range of -60 °C to -100 °C. The rubber becomes fragile and mills easily into very fine particles using ball or hammer milling. The high consumption of both energy and liquid nitrogen make the process very expensive.

Cryogenic techniques can also be used to produce crumb. With these, tyre fragments are cooled, usually using liquid nitrogen, to make them brittle. They can then be much more easily reduced to powder. Such processes are rare in the EU but common in the USA where the price of refrigerants is much lower.

2.2.11 Microwave Method

This is used to cleave carbon-carbon bonds. Waste tyres and rubber material can be reclaimed without depolymerization to a material capable of being re-compounded and re-vulcanized with physical properties equivalent to the original vulcanizate. This route provides an economical and environmental sound recycling method for waste tyres. Furthermore, this process can produce products similar to virgin rubber. It has been found that the tensile property of devulcanized rubber and virgin rubber blend is almost comparable [Hunt 1994]. The cost of devulcanized hose and inner tube material by microwave method is only a fraction of the cost of the original compound. The transformation from waste to refined stock ready for remixing takes place in only about five minutes with usually 90–95 % rubber recovery [Zanetti 2004]. Therefore, the microwave technique is a unique reclaiming process with regards to product properties and process swiftness.

2.2.12 Thermal plasma and nanomaterials

Plasma is one of the four fundamental states of matter besides solid, liquid, and gas, and they are closely relevant to the human life and modern industry. Plasmas resulting from ionization of neutral gases, generally contain an equal number of positive ions and negative electrons (negative ions in some cases), in addition to neutrals, metastable, excited atoms or molecules, reactive radicals, ultraviolet light, and strong electric

field. According to the flexible reactivity of the species in plasmas, the gas-based reactive plasmas are widely used in manufacturing industries such as surface modification of materials, surface processes in the integrated circuits processing [Lieberman 2005].

Over the past decades, a new branch of plasma research, the nanomaterial (NM) synthesis by plasma-liquid interactions (PLIs), is rapidly raising, mainly due to the recently developed various plasma sources operated from low to atmospheric pressures. In the PLIs, plasmas are over or inside liquids, providing plasma-liquid interfaces where many physical and chemical processes can take place, and these processes can be used to synthesize various NMs.

Thermal plasmas, normally generated by DC (direct current) arc or inductively coupled RF (Radio Frequency) discharge, can be described as a high enthalpy flame with extremely high temperature fields (1,000~20,000 K) and a wide range of velocity fields from several m/s [Boulos 1994, Fauchais 1997, Raizer 1999, Pfender 1999, Boulos 1985] to supersonic values [Heberlein 2002, Pateyron 1996].

Devices for plasma synthesis may be grouped by temperature, gas pressure, frequency or the existence of electrodes or not. Fundamentally, one finds high temperature processes, where temperatures significantly above 1,000 K are observed and low temperature processes with temperatures below 1,000 K. In most cases, high temperature processes are connected to higher gas pressures as compared to low temperature processes working at reduced gas pressure. Except for a few very special designs, low temperature processes are not using electrodes.

Carbonaceous materials, such as CNTs, carbon black and nano-metal particles encapsulated in a carbon cage, can also be produced by transferred DC arc discharge as well as other types of torches. However, it should be noted that the properties of produced carbonaceous materials depend on the used plasma torch systems. Based on these review results, it can be concluded that the advantages of thermal plasmas, such as, high enthalpy flows combined with a rapid quenching rate, can be very promising in the synthesis of not only a single phase material but also binary or higher nano-materials. [Vollath 2008a, Vollath 2008b]

2.3 Energy and material recovery

In light of the overall environmental impact along with the drive towards energy and material conservation, new waste tyre disposal options are being developed and implemented. Material and energy recovery through process, such as pyrolysis, can significantly address the waste tyre disposal problem. Possible waste tyre treatment routes within current energy sector are shown as follows. Technologies for managing scrap tyres:

- Co-combustion materialised within coal and wood boilers, cement kilns and the latest plasma reactors;
- Incineration carried out within grate-based or fluidized bed incinerators;
- Mechanical processes (e.g. shredding, granulation or crumbing) are required to mill waste tyres and obtain powder or granules with a specific configuration by using various techniques such as

mechanical milling, cryogenic milling and de-vulcanization processes at ambient or cryogenic conditions (de-vulcanization processes are rarely used because of their high operating costs);

- Pyrolysis based on conventional or microwave heated up method;
- Gasification;
- Combination processes.

2.3.1 Thermal Treatment

The thermal treatment processes encompass combustion (incineration), gasification and pyrolysis of waste tyres, with the following advantages [Anonym 2006]:

- The volume of waste can be reduced by more than 90 %.
- Net energy production with possible material recovery.
- Destruction of organic substances which are harmful to human health.

The following difficulties are associated with the thermal treatment of waste tyres [Anonym 2006]:

- Disposal of ash: Lead and cadmium salts used as stabilisers during tyre production remain as ash causing disposal problems.
- Toxic gases: Burning of tyres produce toxic gases such as SO₂, H₂S, HCl, HCN and these require further treatment.
- Soot: Incomplete burning of waste tyres produces soot. This has a much higher heating value than municipal refuse, so requires further combustion and hence requires higher flame temperatures.
- Appropriate incinerators: To address the challenges such as higher temperatures, minimal oxygen conditions and corrosive action of the gases. Appropriate materials of construction are required.

2.3.2 Incineration

A typical waste tyre incineration process flow diagram is shown as follows. The scrap tyre feedstock incineration process:

- Feedstock – whole or shredded tyres;
- Incinerator – generated residue – ash;
- Boiler – generated residues: flue gas /required fly-ash removal within cyclone or filter separator and additives/ before left to chimney;
- Steam – as work medium;
- Steam turbine - generated power and heat – energy supplied to grid and DH (District Heating system).

The use of waste as a supplementary fuel in power plants offers many advantages and drawbacks as shown in Tab. 2.

Advantages	Disadvantages
Maximum heat-recovery	Large capital-investment
Low air-pollution emissions	Need for flue-gas cleaning
Environmentally-acceptable process	Relatively high operating cost
Reduced power-production costs	Skilled labour is required to operate the system

Table 2. Incineration benefits analysis

2.3.3 Pyrolysis and waste tyre disposal

Pyrolysis of scrap or waste tyres (WT) is an attractive alternative to disposal in landfills, allowing the high energy content of the tyre to be recovered as fuel. Using tyres as fuel produce equal energy as burning oil and 25 % more energy than burning coal. [Anonym 2015]

An average car tyre is made up of 50-60 % hydrocarbons, resulting in a yield of 38-56 % oil, 10-30 % gas and 14-56 % char. The oil produced is largely composed of benzene, diesel, kerosene, fuel oil and heavy fuel oil, while the produced gas has a similar composition to natural gas. The proportion and the purity of the products are governed by two major factors: [Jidgarnka 2006]

- 1.Environment (e.g. pressure, temperature, time, reactor type)
- 2.Material (e.g. age, composition, size, type).

As car tyres age, they increase in hardness, making it more difficult for pyrolysis to break the molecules into shorter chains. This shifts the yield composition towards diesel oil which is composed of larger molecules. Conversely, an increase in temperature increases the likelihood of breaking the molecule chain and shifts the yield composition towards benzene oil which is composed of smaller molecules. [Jidgarnka 2006] Other products from car tyre pyrolysis include steel wires, carbon black and bitumen. [Roy 1999]

Although the pyrolysis of WT has been widely developed throughout the world, there are legislative, economic, and marketing obstacles to widespread adoption. [Daniel Martínez 2013] Oil derived from tyre rubber pyrolysis contains high sulphur content, which gives it high potential as a pollutant and should be desulfurized. [Choi 2014]

A number of prototype and full-scale pyrolysis plants specialized in carbon black production have successfully established across the world, including the United States, France, Germany and Japan. Because carbon black is used for pigment, rubber strengthening and UV protection, it is a relatively large and growing market. Pyrolysis plants specialized in fuel oil production is not an implausible concept. However, as profits of such ventures come from the added value between the production and distillation of oil, there is little profit without vertical integration in the oil industry. The inconsistency of the feedstock makes it very difficult to control the uniformity of the products and makes oil companies hesitant to purchase oil produced via pyrolysis. Finally, the cost of producing oil through conventional means is generally less expensive than this alternative. To date, there is no known commercially profitable standalone pyrolysis plant that specializes in oil production. [Jidgarnka 2006] However, with funding to upgrade pyrolysis oil to light fuel grade, this may be possible. Nevertheless, pyrolysis is a valuable method for disposing waste tyres. [Ringer 2006]

2.3.4 Pyrolysis potential of Scrap Tyres

Pyrolysis of scrap tyres offers an environmentally and economically attractive method for transforming waste tyres into useful products, heat and electrical energy. Pyrolysis refers to the thermal decomposition of scrap tyres either in the absence or lack of oxygen. The principal feedstocks for pyrolysis are pre-treated car, bus or truck tyre chips. Scrap tyres are an excellent fuel because of their high calorific value which is comparable to that of coal and crude oil. The heating value of an average size passenger tyre is between 30 – 34 MJ.kg⁻¹. Pyrolysis is the most recommended alternative for the thermochemical treatment of waste tyres and extensively used for conversion of carbonaceous materials in Europe and the Asia-Pacific. Pyrolysis is a two-phase treatment which uses thermal decomposition to heat the rubber in the absence of oxygen to break it into its constituent

parts, e.g., pyrolysis oil (or bio oil), synthetic gas and char. Cracking and post-cracking take place progressively as the material is heated to 450-500 °C and above.

2.3.4.1 Process Description

The pyrolysis method for scrap tyres recycling involves heating whole or halved or shredded tyres in a reactor containing an oxygen free atmosphere and a heat source. In the reactor, the rubber is softened after which the rubber polymers disintegrate into smaller molecules which eventually vaporize and exit from the reactor. These vapours can be burned directly to produce power or condensed into an oily type liquid, called pyrolysis oil or bio oil. Some molecules are too small to condense and remain as a gas which can be burned as fuel. The minerals that were part of the tyre, about 40 % by weight, are removed as a solid. When performed well a tyre pyrolysis process is a very clean operation and has nearly no emissions or waste. The heating rate of tyre is an important parameter affecting the reaction time, product yield, product quality and energy requirement of the waste tyre pyrolysis process. If the temperature is maintained at around 450 °C the main product is liquid which could be a mixture of hydrocarbon depending on the initial composition of waste material. At temperature above 700 °C, synthetic gas (also known as syngas), a mixture of hydrogen and carbon monoxide, becomes the primary product due to further cracking of the liquids. Pyrolysis process of the scrap tyre feedstock and 3 products:

- Scrap tyre feedstock to pyrolysis reactor – partly solid product (1) - char
- Condenser – partly liquid product (2) - oil
- Final output – partly gaseous product (3) – syngas.

The nature of the feedstock and process conditions defines the properties of the gas, liquid and solid products. For example, whole tyres contain fibres and steel while shredded tyres have most of the steel and sometimes most of the fibre removed. Processes can be either batch or continuous. The energy required for thermal decomposition of the scrap tyres can be in the form of directly-fired fuel, electrical induction and or by microwaves (like a microwave oven). A catalyst may also be required to accelerate the pyrolysis process.

2.3.4.2 Useful Products

The high acceptance of pyrolysis for the treatment of scrap tyres is due to the fact that the derived oils and syngas can be used as biofuels or as feedstock for refining crude oil or chemical products. The pyrolysis oil (or bio oil) has higher calorific value, low ash, low residual carbon and low sulphur content.

The use of pyrolysis oil in cement kilns, paper mills, power plants, industrial furnaces, foundries and other industries is one of the best uses of scrap tyres. Pyrolysis of scrap tyres produces oil that can be used as liquid fuels for industrial furnaces, foundries and boilers in power plants due to their higher calorific value, low ash, residual carbon and sulphur content.

The solid residue, called char, contains carbon black, and inorganic matter. It contains carbon black and the mineral matter initially present in the tyre. This solid char may be used as reinforcement in the rubber industry, as activated carbon or as smokeless fuel.

3 CONCLUSIONS

Energy recovery: Waste tyres can be utilised as a fuel source – secondary energy carrier or raw material. Tyres produce the same amount of energy per unit mass as oil and slightly more than coal [Anonym 2007]. Hence, tyres can be used as an efficient fuel for industrial processes such as power plants with minimum negative environmental impact compared to coal. In most cases tyres are shredded but the use of whole tyres is also possible with large machinery. The presence of steel belts hinders the use of whole tyres. The Shredding of whole tyres and removal of wires can be integrated as part of the process. Energy from the direct combustion of waste tyre can be utilized in metal works, paper mills, and tyre factories and on a smaller scale, in farms, greenhouses and sewage treatment plants.

Tyre recycling represents an untapped opportunity, that may prove a success if processing costs do not become prohibitive. Europe's tyre waste production represents 3 million tonnes per year. Currently 65 % to 70 % of used tyres end up in landfills. They are not only causing environmental damage, but moreover a loss of added value in the form of new products that recycling can generate. Tyres offer recycling potentials because they have a better heating value than biomass or coal, and they contain a high content of volatile gasses. They can therefore be an interesting source of synthetic fuels, also called *synfuels*.

We are looking into the exploitation of the formed char to produce other valuable materials – activated carbon or nanomaterials, whose are commercially attractive today. Turning tyres into gas for energy and new valuable materials or commercial by-products. Such by-products are what add the most value to the recycling process. Solid carbon is collected after the gasification as a basis for the productions of these by-products. Recycling tyres to create fuels only is not promising, but having a valuable nanomaterial as an added by-product is a good choice. "Nanomaterial based on carbon" is one of the materials of the future, it is used in metallurgy, in ceramics, and in a variety other products. [Vollath 2008a, Vollath 2008b]

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