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### ABSTRACT

Scrap tires are a burdensome and common kind of waste. Almost 1.5 billion tires are produced each year and each tire produced will eventually join the waste stream. According to European Union regulations, the disposal of waste tires is prohibited; as an alternative they should be recovered and recycled. Pyrolysis allows the dissolution of the waste and it also produces useful by-products. In this process gas, liquid and solid phases are formed. Pyrolytic gases have high heating value, about 30-40 MJ/Nm<sup>3</sup>. The energy obtained from combustion of the pyrolytic gas is enough not only to perform the pyrolysis process but it can also be utilized for other applications. However, there is a big challenge: the concentration of SO<sub>2</sub> in the flue gases is greater than regulatory limits. Similar situations could also arise with HCl, NO<sub>X</sub> and heavy metals. In order to meet regulatory requirements and maintain optimum pyrolysis, gas cleaning methods will be needed in order to remove those substances from the exhaust gases formed during waste tire pyrolysis. The main aim of this article is to review the properties of pyrolysis gas for energy recovery because it is a good gaseous fuel. In addition, possible implications will be identified.

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### 1. Introduction

Nowadays energy supply and environmental pollution are important international issues. The vast quantity of used and waste tires represent a particular problem. Each year about 1.5 billion tires are produced around the world, which correspond to an estimated 17 million tonnes of used tires. In 2013, the used tires in European Union countries were estimated at 3.6 million tonnes [1]. In the U.S. about 4 million tonnes was generated in 2015 [2]. China, the European Union countries, the USA, Japan and India produce the largest amounts of waste tires - together almost 88% of the total [3]. Most of them are recycled or recovered [1]. Other methods of waste tire treatments, like gasification or pyrolysis, are still underutilised but looking at stricter EU environmental regulations, the energy crisis, fuel depletion and an increasing number of investments in pyrolysis plants, they seem to be the future for waste tire treatment. Unfortunately, in some countries, waste tires are still being dumped. Disposal of waste tires is very problematic and dangerous for the environment and human health.

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http://dx.doi.org/10.1016/j.energy.2017.05.042 0360-5442/© 2017 Elsevier Ltd. All rights reserved. Tires properties, like resistance to mechanical damage, long life and safety, regardless of weather conditions, make disposal very difficult. The rubber is abrasion and water resistant. It is also resistant to heat, electricity, many chemicals and bacteria. Microorganisms need more than 100 years to destroy tires [4]. Moreover, spent tires are bulky waste. Waste tires dumps are also a high threat to the environment and human health because of the risk of fire and because they are habitats for mosquitos and rodents, which are strongly associated with many diseases.

Uncontrolled burning of tires generates smoke, oil and other toxic substances that pollute the atmosphere, soil, surface water and groundwater [5–7]. Apart from the problems with waste tires mentioned above, the tires also provide large opportunities for resource conservation, because they are a source of great potential for valuable materials and fuels [8].

Increases in the quality of life and the general development in countries are leading to a growth in the number of car users. According to the statistics, the number of cars is increasing continuously. In Europe it could reach 347 million by 2025 (compared with 322 million in 2014). In China and India, the numbers are respectively 332 and 69 million in 2025 (compared with 107 and 28 million in 2014). In the latter cases, this represents more than a two-fold increase [9]. Additionally, the number of trucks also is

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growing quickly, because this kind of vehicle delivers materials and products, which people around the world – especially in developing countries - need more and more every year. It should be noticed, that truck tires have quite different qualities, because they must be more durable than the tires of cars and so their disposal could even be more difficult.

The management of waste tires should follow the generally accepted hierarchy: prevention, minimization of waste, reuse, recycling, energy recovery and - eventually - landfilling. Applying the above-mentioned options could help to reduce the negative impact of waste on the environment. The legal prohibition of tire stockpiling in landfills in European Union counties was introduced by a Waste Landfill Directive in 1999 [10]. Effects are impressive. In 1996, about 50% of waste tires were stored at landfill sites, and in 2010 only 4% [11]. Disposal of tires in landfill sites is also prohibited in 11 states in the U.S. Some states have emphasized the use of waste tires as a fuel supplement, while others, such as Arizona, place a very heavy emphasis on recycling tires through use as rubberized asphalt [12]. In 1990, about a billion scrap tires were in stockpiles in the U.S. By 2015, over 93% of those tires have been cleaned up [2]. Sienkiewicz et al. reviewed the methods of waste tires utilization in the European Union. They focused on legislation and short described and compared available methods such as retreading, energy recovery, pyrolysis, and product and material recycling [7]. Pyrolysis is considered one of the most promising methods for waste tire recycling and/or energy recovery and was considered several times. Martinez et al. widely described the waste tires pyrolysis parameters and their influence on product vields and composition. They also studied in detail the pyrolysis oils composition and properties. However, less attention was paid to the char and pyrolytic gas [13]. On the other hand, Williams more accurately described the types of reactors used in pyrolysis of waste tires. He also did not delve into the topic of pyrogas [14]. It is worth noticing, that this process, carried out in appropriate conditions, gets rid of problematic waste and obtains: 1) valuable liquid chemicals, 2) good quality char (raw material for activated carbon production), 3) gaseous fuels, which provide enough energy to run the process and additionally produces electricity. However, there are some important challenges faced by scientists and engineers: 1) the high sulphur content in pyrolysis products, 2) economic viability and 3) emissions standards, which must be fulfilled. The most important aim of this article is to accurately describe the properties of pyrolytic gas with a particular consideration for its use in energy recovery, since it is a gaseous fuel with good properties. However, possible problems related to this will also be addressed especially in the context of air emissions.

### 2. Characteristics of tires

### 2.1. Composition

A typical tire consists principally of three kinds of materials: *rubber mixtures, metal and textiles.* Each material has specific properties, which used in the right combination provide the tire with the required strength and flexibility. Fig. 1 compares the contents of typical materials used in car tires and truck tires manufactured in Europe.

The rubber mixtures represent the main component of vehicle tires. They consist of natural and/or synthetic rubber, carbon black, amorphous silica, vulcanizing agents and a lot of additives. It can be said that more than one hundred compounds can be added to the tire depending on the specific use to be given to the tire [13]. Natural rubber is obtained from the sap of the Hevea brasiliensis tree and despite the invention of synthetic rubber, natural rubber is characterized by unique properties and it still is the most important element in the production of tires. Synthetic rubber is derived from petroleum-based products. The most widely used kinds of synthetic rubber are butyl rubber and styrene-butadiene rubber. Besides the rubber, important ingredients of the rubber mixtures are carbon black and amorphous silica, that make the tire durable and resistant to wear and tear [15]. Vulcanisation is a chemical process for converting natural rubber or related polymers into more durable materials via the addition of sulphur (including compounds). These additives modify the polymer by forming cross-links (bridges) between individual polymer chains. Vulcanised materials are less sticky and have better mechanical properties. Therefore, another two important substances appearing in the composition of rubber mixtures are sulphur (also its compounds) and zinc oxide, which are commonly used as vulcanising activators.

The second type of material used for the production of tires is metal. Usually it is high quality steel wire. The coating materials and activators includes brass, tin and zinc. The purpose of the metal is to provide rigidity and strength in tires [15].

The last type of material used in the pneumatic tire is textiles. Reinforcing fabrics are used to lend structural strength to the carcasses of car tires [15]. They could be synthetic or natural. The most widely used are polyester, rayon or nylon.

### 2.2. Structure



Each tire is a product with a complex structure too. The most common types of tire structure are diagonal (cross-ply), bias-belted and radial, but almost 80% of all tires sold are radial [14]. A typical

Fig. 1. Composition of tires [7].

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