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Opportunities and barriers for producing high quality fuels from the pyrolysis of scrap tires

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ABSTRACT

The $7 \cdot 10^6$ t of waste tires that are generated yearly represent for a potential source of fuels considering its composition, rich in C and H, and its chemical features. Waste tires can be recycled through several processes aiming for either material, energy, or chemical product recovery. In this work we review the current status of these valorization pathways, with a particular focus on pyrolysis, its main products and their characteristics. Despite the extended reviews on the pyrolysis of tires, scarce material is available regarding the possibilities that scrap tires pyrolysis oil (STPO) offers and its limitations. STPO is both the most economically and energetically attractive product, and its composition (as obtained by different authors) is analyzed in this work, finding that the main barriers to solve for its direct implementation are (i) high sulfur content, (ii) high content of aromatics and (iii) high proportion of heavy molecules (> 350 °C). From an industrial perspective, a sequential 2-stage hydrotreating–hydrocracking strategy has been proposed for STPO upgrading in order to simultaneously overcoming all these limitations and produce high quality fuels.

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1. Introduction

The necessity to satisfy the energetic demand associated to developed countries and the growing demand from developing countries is a mayor political issue within the present socio-economical world scenario. Considering the depletion of oil, the utilization of alternative energy sources becomes a major issue. Refinery industry is progressively adapting to lower-price heavier feedstock due to the depletion of the higher-price and lighter one, so that these adaptations could be used for feeding more unconventional feeds progressively; like wastes and biomass. Moreover, fuels need to comply with increasingly severe restrictions regarding their composition in terms of sulfur, nitrogen, aromatic and olefin content.

Waste refinery is defined as the group of thermo-chemical operations aiming for the production of fuels and chemicals from the valorization of wastes (tires, plastics, sewage sludge, etc.) or secondary refinery streams. Waste refinery requires adaptations or completely new technologies to the ones already in use in the refinery, and hence, the implementation of these processes involves progressive development of reactors, kinetic models, catalysts, catalyst deactivation models and other process innovations.

Within the waste refinery concept, waste tire valorization is a major driving force for research and innovation. Based on an average rate of waste tires of ca. 6 kg$\cdot$(habitant$\cdot$year)$^{-1}$ [1], $17\cdot10^6$ t of waste tires were generated in 2012, which correspond to $2.8\cdot10^9$ tires. Other estimations based on the 2 wt% of the total waste, compute a rate of waste tire disposal of $7\cdot10^6$ t year^{-1} [2], from which $1.15\cdot10^6$ t correspond to the European Union (EU), while other estimations even double this amount [3].

An increase of the Gross Domestic Product (GDP) of a country also fosters growing vehicle demand as well as tire substitution for safety issues. This trend occurs in a greater extent than that of the extension of the tire lifetime [4]. The significant tire consumption increment in Asia and Oceania in the last years will make these regions the main waste tire source of the next two decades, being China the main producer with $5.2\cdot10^6$ t in 2010 (accounting for 60 wt% of the total) [5].

In the EU, waste suppression and vehicle life-cycle-end directives generate the necessity to valorize no less than 40 wt% of tires, whose endpoint is otherwise to be dumped in landfills. As a representative example, Spain has its own rules concerning out-of-use waste tires management (Royal Decree 1619/2005), which is also subject to the rules established in the Royal Decree 1383/2002, about management of vehicles at the end of their useful life-cycle. In a broader context, tire management is included within the National Integrated Plan of Wastes for the 2008–2015 period, and regulated by the 22/2011 Law from July 28th, of Wastes and Polluted Soils, which replaced the previous 10/1998 Wastes Law from April 21st, and is adapted to the Spanish 2008/98/CE directive about wastes.

European regulations define end-of-life tires as those which, according to their physical state and considering current security regulations, should be intended for recycling or valorization or could not continue in service without being subjected to techniques that extend its useful life. They are also considered as such chambers and tires disposed by their owner, even though if they do not comply with the previously described requirements. The compounds present in tires are non-biodegradable, and due to their shape and mechanical features they have low apparent density and difficult compaction.

Many factors have driven attention towards the valorization of petroleum-derived wastes like plastics [6], and particularly tires, such as: (i) the environmental damage that is caused by uncontrolled disposal of this type of polymer waste, (ii) the non-biodegradability of tires, (iii) the increasing demand for recycling hydrocarbons, and (iv) its high calorific value, which could allow for its use as a fuel.

Fig. 1 shows the valorization pathways available for tires, and the recovered products that can be recycled to each petrochemical industry manufacturing stage. Even though nowadays energetic recovery is the most common means for tire recycling, the previously detailed legal regulations encourage for other recycling alternatives. Refinery processes allow for obtaining synthetic monomers that can be further polymerized for obtaining virgin polymers that, after being processed (vulcanized) with the required additives to confer them with the required mechanical properties, give way to the final tire product. Once tires are no longer in use, and providing they maintain their original structure intact, they can be directly reused, as a primary recycling strategy. When their physical condition is too damaged, tires can be grinded through different mechanical processes, in such a way that the rubber structure remains unchanged and the polymer can be recovered. Complete destruction of the tire rubber structure requires of different chemical processes, allowing for the recovery of the original monomer (that can be subjected to vulcanization again), and a liquid fraction that shows great potential towards being used as a fuel, and can be further co-processed in refineries, aiming for adapting its composition and properties to commercial fuel requirements.

Within this general context, this work compiles and summarizes the currently available tire recycling strategies, paying particular attention to pyrolysis, as a promising alternative arousing from the necessity to achieve a more sustainable and "greener" energetic scenario. As a complement to the extensive work reported on tire pyrolysis, this paper aims to fill the gap existing on the literature regarding the possibilities for exploring

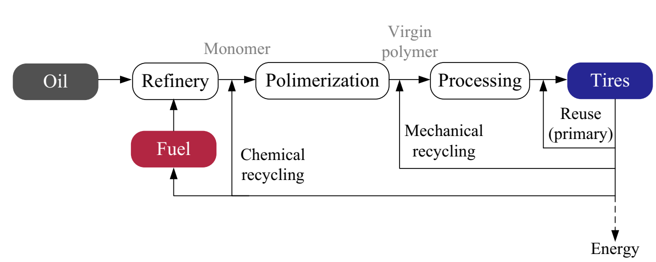

Fig. 1. Overview of integral valorization pathways available for petroleum derived wastes.