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A review on the demineralisation of pre- and post-pyrolysis biomass and tyre wastes

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ABSTRACT

Pyrolysis is an attractive technology to convert low-cost carbonaceous waste materials into fuels, energy and other value added products goods. During pyrolysis, the inorganic minerals present in the feedstock can cause problems to the equipment and give side reactions. Besides, the minerals present in the chars can hinder their possible applications. Therefore, it seems necessary to eliminate said contaminants in order to valorise the aforementioned goods. Demineralisation is a process widely used for purifying materials that are contaminated with inorganic matter. Although this technique is commonly used with waste materials that will undergo pyrolysis, or the products obtained from it, the studies analysing this practise are rather scattered.

The aim of this paper was to compile and review the current literature concerning the demineralisation of carbonaceous waste (tyres and lignocellulosic biomass) materials. The chemistry involved, feedstock type and the effect of performing the purifying step before or after pyrolysis were addressed in this work.

The review revealed that biomass samples should be demineralised before pyrolysis in order to affect not only the char but also the bio-oil quality. Depending on the form in which the minerals are linked to the structure, the solvent chosen will vary (from water to strong acids). However, water is the most popular option due to its price and easy disposal. In tyres, demineralisation should be performed after pyrolysis using strong acid and subsequently base. Due to the crosslinked chemical structure, rubber is highly resistant to chemicals thus the pre-treatment has to be avoided.

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1. Introduction

We live in a consumer society where due to the fast way of life, products have a very short service life. The world population is increasing together with the lifestyle development and urbanisation. Urban area dwellers produce higher waste levels than rural area inhabitants, who tend to reuse and recycle more (Hoornweg and Perinaz, 2012). Therefore, the waste production rate is increasing and will continue doing so in the future.

As a case in point, due to the high amount of cars required nowadays, >1.5 billion tyres are produced per year in the world (ETRMA, 2014; JATMA, 2016; RMA, 2015), which sooner or later they will become a waste (Karakurt, 2014). Although tyres do not present a danger to the health on their own, the inappropriate disposal and mismanagement of big amounts can cause serious problems not only to the environment but also to human beings.

Tyres are thermoset materials that cannot be melted and reprocessed and are infusible, insoluble and have very high strength and resistance to abrasion, heat, chemicals and degradation. These properties make waste tyres highly difficult to recycle. Therefore, the handling of used tyres is gaining a lot of attention (Torretta et al., 2015). Due to the waste management legislation becoming more and more severe, landfilling of waste tyres is getting banned in numerous countries (EEA, 2009). There are several alternatives for tyre recycling such as reclaiming and retreading, but they have limited applicability. Recycling cannot address the full problem, as it is a very high cost process resulting in products with questionable characteristics (Antoniou et al., 2014).

Feeding a society that does not stop growing is also a challenge from the point of view of waste as crop residues are the main source of inedible phytomass (Smil, 1999).

Biomass is a non-fossil biogenic solid product generated by natural and anthropogenic processes. Biomass varieties can be classified according to their biological diversity, source and origin in: wood and woody biomass, herbaceous and agricultural, aquatic, animal and human wastes, contaminated biomass and industrial wastes (semi-biomass) and mixtures (Vassilev et al., 2010). Waste biomass is derived from several processing methods applied to obtain biomass products (Easterly and Burnham, 1996). Biomass wastes have been used all over the world since the old times in several applications, such as farmyard manure, basketing, mat making, and so on. In modern times, the development of synthetic fibres, chemical fertilisers, etc. have replaced the use of this residue (Prasad and Power, 1991), increasing the amount of biomass left in the fields.

Aside from the waste disposal matter, an additional global concern is the energy crisis. The energy content of waste can be recovered by means of either biological processes (e.g. anaerobic digestion) or thermo-chemical processes (combustion, pyrolysis or gasification). Owing to its simplicity and environmental benefits, pyrolysis is proving to be a promising form of waste recycling, with the production of potentially valuable products (Collard and Blin, 2014; Danon et al., 2015b). Pyrolysis is an attractive solution for reducing waste volume, to conserve landfill space while allowing energy recovery. It consist on the thermal decomposition of a material in the absence of oxygen (inert atmosphere) to produce gas (non-condensable low-molecular-volatiles including C_1-C_6 hydrocarbons, hydrogen, CO, CO_2 etc.), oil (hydrocarbon liquid containing water) and char (pyrolytic solid) fractions (Wampler, 1995). Yields and composition of pyrolysis products are affected by the conversion conditions and the chemico-physical properties of the raw material, type of reactor, residence time, etc. (Williams, 2013). For example, fast pyrolysis (high heating rates and short vapour residence times) is preferred to maximise the oil yield (Bridgwater, 2012a), opposed to slow pyrolysis which enhances char production (Hodgson et al., 2016).

For pyrolysis to be an attractive process from a commercial point of view, all the products obtained should have a market. The gas fraction can be used as a fuel in industrial combustion processes. For instance, it can be used to partially fulfil the energy requirements of the pyrolysis process itself. The liquid fraction can also be used as fuel (due to its high calorific value) or as a potential source for valuable chemical such as: benzene, toluene, xylene or limonene (Antoniou and Zabaniotou, 2013). These chemicals can be used as precursors for the manufacture of chemicals with more complex structure, as solvents in laboratory and industrial applications or in the case of limonene even as cleaning or fragrance agent (Danon et al., 2015b). The gas and liquid fractions have a potential market however, the solid product has to be upgraded and valorised so it can be used for more demanding applications, for example as reinforcing filler or activated carbon. In its raw form, char consist of a carbon matrix containing most of the inorganic compounds present in the raw material (ash) and some condensed organic by-products generated during secondary reactions in the reactor.

There are different waste materials; thermoplastics, tyres and biomass that are appropriate for undergoing pyrolysis, due to their combustible properties and high volatile matter content and because they are rich in long polymer chains that can be easily cracked into smaller molecules (hydrocarbon gas and pyrolysis oil) (Bernardo, 2011).

Thermoplastics pyrolysis char yields are so low that so far no work has been published (according to our knowledge) on polymer demineralisation, thus it will not be further analysed in this review.

During pyrolysis of waste tyres, the chemical additives in the sample evaporate first and then rubber fraction devolatilises by depolymerisation/condensation, leaving only the carbon black and minerals (Danon et al., 2015a). The gas and TDO (tyre derived oil) originate from the volatiles fraction emerging from the process, while the char consists of the solid fraction (Martinez et al., 2013). The solid obtained (commonly known as pyrolytic char) is a heterogeneous, porous structure with a low surface area, mainly made of carbon black added during processing. The char is much coarser than the carbon black added to the tyre during processing, due to the fact that volatile products formed during pyrolysis tend