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Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review

Gartzen Lopez*, Maite Artetxe, Maider Amutio, Javier Bilbao, Martin Olazar

Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644-E48080, Bilbao, Spain

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A B S T R A C T

The continuous increase in the generation of waste plastics together with the need for developing more sustainable waste management policies have promoted a great research effort dealing with their valorization routes. In this review, the main thermochemical routes are analyzed for the valorization of waste polyolefins to produce chemicals and fuels. Amongst the different strategies, pyrolysis has received greater attention, but most studies are of preliminary character. Likewise, the studies pursuing the incorporation of waste plastics into refinery units (mainly fluid catalytic cracking and hydrocracking) have been carried out in batch laboratory-scale units. Other promising alternative to which great attention is being paid is the process based on two steps: pyrolysis and in-line intensification for olefin production by means of catalytic cracking or thermal cracking at high temperatures.

1. Introduction

Plastic production has steadily grown up from the start of its massive production in the 1930's to a global value of 311 million tons (MT) in 2014, with the current annual growth rate being of around 4% [1]. Plastics have become a basic product that guarantee the modern standard of quality of living. The excellent properties of plastics in terms of low cost of manufacturing, light weight and durability have enhanced their applications and led to a displacement of traditional materials, such as wood, metals and ceramics [2].

Moreover, the development of new plastics together with composite materials have extended even more their applications. Fig. 1a shows the current distribution of plastic demand in Europe according to their applications, and Fig. 1b shows the distribution of the demand according to their nature. As observed, polyolefins, namely, high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP), are the most common plastics and account for around half of the overall production.

However, the distribution of plastic usage time clearly involves a significant challenge of sustainability because many applications are characterized by a short life. Thus, the most common application of plastics is packaging and this means a significant fraction of the plastics produced have a useful life below one month [3]. The European Union (E.U.) produced 47.8 MT of plastics in 2014, of which 25.8 MT of post consumer plastics were recovered in the waste streams. Currently, the main application of these plastic wastes is energy recovery (39.5%), with the fractions recycled (29.7%) and that sent to landfill (30.8%) being similar [1]. Although plastic landfill has been steadily reduced in the EU in recent years, the present scenario is far from being satisfactory. Furthermore, the situation of plastic waste management in developing countries is not promising.

In order to minimize plastic wastes landfill, several valorization alternatives have been proposed, which range from primary routes of direct recycling to quaternary routes of energy valorization [4,5]. This review focuses on tertiary (chemical) valorization routes aimed to produce fuels and chemicals from waste plastics. The production of fuels and chemicals has been addressed following two main strategies; the development of specific pyrolysis processes [2,6–14] and the integration of waste plastics or plastic-derived products in refinery units [15–17]. Another relevant tertiary valorization route of waste plastics lies in the gasification aimed at the production of a gaseous stream for energy or synthesis purposes [18–22]. More recently, another process based on pyrolysis and reforming strategies has been proposed for H_2 production [23–28].

This review has been limited to polyolefins due to practical reasons. On the one hand, this family of polymers is the most abundant one and, on the other, they have a similar composition and so the same valorization routes may be applied to all of them. This is not the case for other massively produced plastics with a similar composition to that of polyolefins (made up of hydrocarbons), as are polyvinyl chloride (PVC) [29], polyethylene terephthalate (PET), polyurethane (PU) and polystyrene (PS). Fig. 2 summarizes the main thermochemical processes proposed in the literature for the valorization of polyolefins.

* Corresponding author.
E-mail address: gartzen.lopez@ehu.es (G. Lopez).

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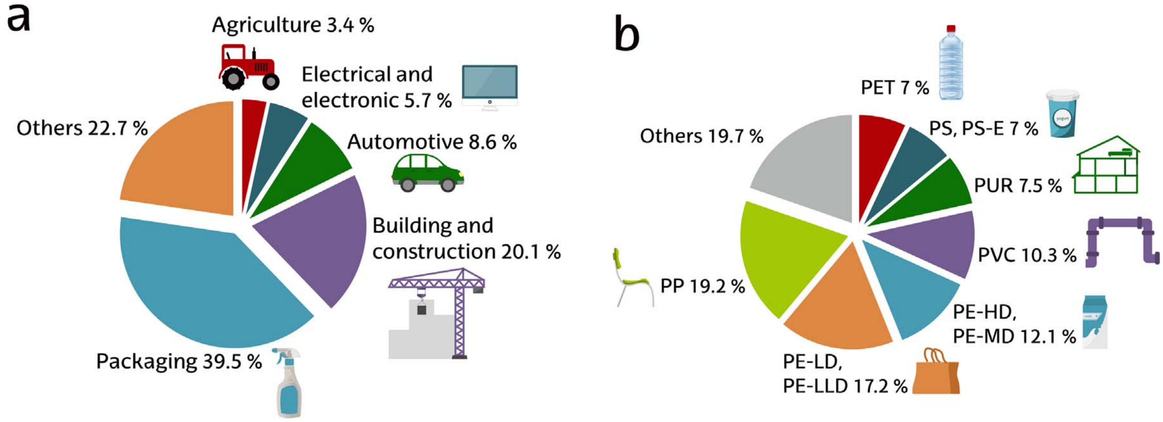

Fig. 1. Current plastic distribution demand in Europe depending on their application (a) and type of polymer (b) [1].

The development of waste plastic valorization routes has to face challenges related to the features of these residues. Thus, the variable contents of impurities or even undesired plastics (such as PVC) can seriously limit their processing. Furthermore, it should be considered that the price of plastic wastes strongly depends on their quality, with those of high purity being very expensive. In addition, the recovered waste plastic market is characterized by a great price volatility [30], which seriously hinders any investment decision. Moreover, the feeding of low quality waste plastics should be carefully addressed when an intensified plastic waste preprocessing is required due to the associated high investment and processing costs. Accordingly, the development of tertiary routes do not depend only on the process yields but also on the capacity for handling low quality waste plastics.

This review focuses on scalable processes aimed at selectively producing specific products of interest, such as light olefins, fuel, aromatics or waxes. A great effort has been made to relate the features of different conversion technologies and processing conditions with the improvement in the yield of the mentioned products of interest. Furthermore, the main studies dealing with the incorporation of plastic wastes in refinery units have also been considered. Accordingly, the main objective of this paper is to provide a critical review on polyolefin upgrading by comparing different valorization routes aimed at the production of fuels and chemicals.

2. Plastic waste management legislation

Although the large amount of plastic waste produced and its low degradability cause serious environmental problems, plastic waste valorization is not specifically addressed by the EU legislation. However, Waste Framework Directive (WFD) [31] and the Directive on Packaging and Packaging Waste [32] regulate plastic waste management.

In Europe, wastes were legislated for the first time in 1975 (Directive 75/442/EEC) with the aim of reducing waste production and its harmfulness [33]. This directive was revised several times [34] and nowadays waste management is legislated by waste framework directive 2008/98/EC [31]. Its main objective is to protect the environment and the human health, for which measures are taken to reduce the adverse impacts of waste generation and management, as well as the overall impacts of resource use. This waste directive includes the novelty of waste hierarchy, establishing the following priority order in waste prevention and management legislation and policy: (i) prevention, (ii) preparing for re-use; (iii) recycling; (iv) valorization; and (v) elimination. Besides, the WFD extended producer's responsibility and set the objective of recycling 50% of the household waste (including plastics) by 2020.

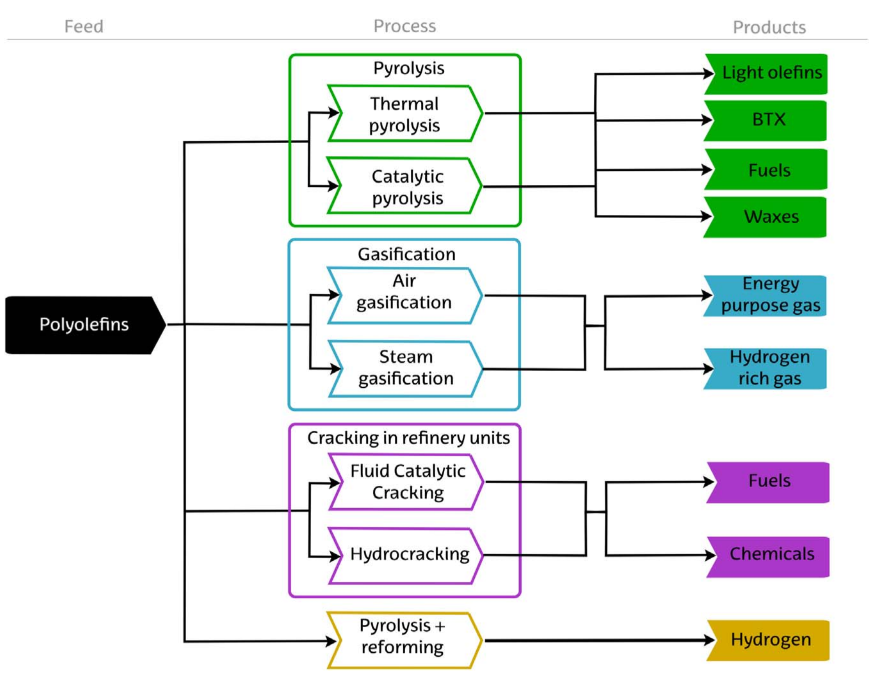

Fig. 2. Main valorization routes of waste polyolefins for the production of chemicals, fuels and syngas.