



# Valorisation of different waste plastics by pyrolysis and in-line catalytic steam reforming for hydrogen production



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## ABSTRACT

The performance of an original two-step reaction system (pyrolysis and in-line reforming) was assessed in the hydrogen production from different plastics (polyethylene, polypropylene, polyethylene terephthalate and polystyrene) and their mixture. The pyrolysis step was performed in a conical spouted bed reactor at 500 °C, whereas the reforming of pyrolysis volatiles was carried out in a fluidized bed reactor at 700 °C. This two in-line reactor configuration was initially developed for the reforming of high density polyethylene pyrolysis volatiles, and this paper describes the influence composition of pyrolysis products derived from different plastics has on the reforming step, conversion, product yields and deactivation behavior. The products formed in both the pyrolysis and the reforming steps were analysed by on-line gas chromatography and micro-gas chromatography. Significant differences in the reforming behaviour of the plastics were observed, with hydrogen productions being higher in the case of polyolefins (from 34.8 to 37.3 wt%) followed by polystyrene (29.1 wt%) and remarkably lower for polyethylene terephthalate (18.2 wt%). Furthermore, the evolution of conversion and product distribution with time on stream was assessed for the different plastics studied and the catalyst deactivation rate was related to the amount and morphology of the coke deposited on the reforming catalyst. It was proven that the features of the reactors used in the pyrolysis and reforming steps are suitable for minimizing operational problems, and therefore operating in continuous regime.

## 1. Introduction

The production of plastic has continuously increased in the last decades, and according to recent estimations the global annual production was of 322 million tonnes in 2015 [1]. This is due to their increasing application in several sectors, such as packaging, building, automotive, electric and electronics and agriculture. Polyolefins represent around half (48.5%) of the overall plastic production, with the other commodity plastics being mainly polyvinyl chloride (PVC), polyurethane (PUR), polyethylene terephthalate (PET) and polystyrene (PS), whose productions account for 10.1, 7.5, 7.1 and 6.9, respectively [1].

Although waste plastic recycling legislation is progressively more restrictive and the potential economic benefits are important [2], the scale up and development of valorisation technologies faces remarkable challenges. Thus, from the total amount of post consumer waste plastics generated in 2014 in the European Union, 69.2% was recovered for energy production and recycling, with the remaining 30.8% being landfilled [3]. Moreover, inadequate waste plastic management causes serious environmental impacts, such as their accumulation in the

oceans leading to marine debris [4]. The uncontrolled incineration of waste plastics is a hazardous source of air pollution, which is responsible for the release of dioxins, furans, mercury and polychlorinated biphenyls [5]. In view of this scenario, there is an urgent need to develop environmentally friendly waste management routes. Amongst these routes, thermochemical ones are regarded as the most promising ones for their full scale implementation [6]. Thus, thermal and catalytic pyrolysis has been widely studied in the literature [7]. Moreover, the incorporation of waste plastics or their derived products (as waxes) into refinery units also represent a potential valorisation route [8]. Therefore, the interest of these processes lies in the selective production of chemicals, monomers and fuels [9]. However, the implementation of pyrolysis technologies is limited by the strong dependence of product characteristics, especially pyrolysis oil, on the plastic composition [10]. Thus, the conversion of waste plastics into gaseous products by gasification processes allows overcoming this limitation and improving the flexibility to treat waste plastics of different composition [11]. Air gasification of plastic wastes allows producing a gas with a low heating value in the 5–10 MJ m<sup>-3</sup> range [12], and fluidized bed gasifiers are the most developed technology [13], in which

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**Table 1**  
Properties of the plastics used.

	High density polyethylene	Polypropylene	Polyethylene terephthalate	Polystyrene	Mixture
Supplier	Dow Chemical	Dow Chemical	Artenius	Dow Chemical	–
Molecular weight (kg mol <sup>-1</sup> )	46.2	50–90	25–30	311.6	–
Polydispersity	2.89	2.0	2.0	2.39	–
HHV (MJ kg <sup>-1</sup> )	43	44	24	40	42
Ultimate analysis (wt%)					
C	85.7	85.7	62.5	92.3	84.4
H	14.3	14.3	4.2	7.7	12.9
O	0	0	33.3	0	2.7

different approaches have been proposed to promote primary and secondary tar cracking [14]. On the other hand, steam gasification leads to a H<sub>2</sub> rich syngas [15], with H<sub>2</sub> productions of up to 16 wt% being obtained under suitable conditions [16]. However, waste plastic gasification faces significant challenges, especially those leading to high tar formation rate [17]. In fact, high tar content in the gaseous products hinders its final utilization in synthesis and energy applications [18].

Pyrolysis-reforming strategy has been proposed as a suitable route to produce H<sub>2</sub> from waste plastics [11], and a wide range of reactor combinations at laboratory scale have been proposed. Thus, the use of two fixed bed reactors at laboratory scale in batch regime is an alternative of simple design and operation [19]. Moreover, the same configuration was also used in bench scale units and in continuous regime [20]. Other authors proposed the use of fluidized bed reactors for the reforming of the volatiles formed in the pyrolysis of plastics conducted in fluidized beds [21] or spouted beds [22]. More recently, the combined production of H<sub>2</sub> and carbon nanotubes over different Ni and Fe based catalysts has also been approached [23].

In the pyrolysis-reforming strategy, the steps of plastics pyrolysis and the in-line catalytic steam reforming of nascent volatiles are performed in two independent reactors, which provides significant advantages, as are: (i) an independent temperature optimization in the pyrolysis and reforming steps may be implemented; (ii) the reforming temperature may be significantly reduced with respect to conventional gasification, which allows minimising catalyst sintering problems; (iii) the direct contact of waste plastic charges and impurities with the reforming catalyst is avoided, and; (iv) the highly active reforming catalyst allows producing a tar free gas. Therefore, H<sub>2</sub> productions above 30 wt% have been reported by different authors in the pyrolysis-reforming of different plastics [11]. Thus, the pyrolysis-reforming of polyolefins, such as high density polyethylene (HDPE) and polypropylene (PP), allowed obtaining H<sub>2</sub> productions of up to 37 wt% [24]. On the other hand the lower H<sub>2</sub> content of polystyrene (PS) leads to lower productions (up to 33 wt%) [25].

The arrangement of two fixed bed reactors for the pyrolysis and reforming steps has been widely used [11]. Nevertheless, the use of fixed bed reactors caused significant operational problems related to the fast catalyst deactivation due to excessive coke formation [26]. The pioneering studies by Czernik and French were performed in a system made up of two fluidised beds, and this combination showed clear advantages for operation with continuous plastic feed [21]. Recently, Barbarias et al. developed a continuous process made up of a conical spouted bed reactor (CSBR) and a fluidized bed reactor (FBR) for the valorisation of HDPE [24]. Therefore, the advantages of the CSBR for the pyrolysis of waste plastics (high heat and mass transfer rates, short residence time and absence of operational problems, such as defluidization) [8] were combined with the suitable performance of the catalytic FBR for volatile steam reforming.

The aim of this paper is to extend the application of the CSBR-FBR configuration to the valorisation of plastics of different composition and plastic mixtures. The main interest of operating with waste plastic mixtures lies in the improvement of this technology with the aim of scaling it up for the valorisation of the plastics contained in the

municipal solid waste (MSW). Thus, feedstock availability for H<sub>2</sub> production is improved and waste collection and separation costs are considerably reduced. However, plastics of different nature in the feed greatly influence the composition of the volatiles formed in their pyrolysis. Therefore, their effect on the subsequent reforming performance needs to be analysed in detail.

## 2. Experimental section

This section describes the characteristics of the plastics and catalyst used. Moreover, the pyrolysis-reforming experimental unit, analytical equipment and the procedures used have also been detailed. Finally, the main reaction indexes have been defined and explained.

### 2.1. Materials

The pyrolysis and in-line reforming of four different plastics was studied: HDPE, PP, PET, PS and their mixture, whose composition (HDPE, 48 wt%; PP, 35 wt%; PS, 9 wt% and PET, 8 wt%) was fixed according to the composition of waste plastics in the MSW. Although there is a high content of polyvinyl chloride (PVC) in waste plastic streams, this plastic was not considered in this study due to the negative effects of chloride in both the experimental unit and the catalyst performance. However, the problems caused by chloride may be minimised by performing a previous pyrolysis step (at 300 °C), in which it is almost fully removed and retained on an alkaline support (such as CaCO<sub>3</sub>) [27]. The main characteristics of the plastics and their mixture used in this study are set out in Table 1. The plastics were directly fed into the reactor in the form of pellets (4 mm), given that no size reduction is required.

The steam reforming catalyst used was a commercial one (G90LDP) developed for methane reforming, and supplied by Süd Chemie. The catalyst has a metallic phase of Ni supported on Al<sub>2</sub>O<sub>3</sub>, which was doped with Ca, and its chemical formulation is made up of NiO (14 wt %), CaAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>. In order to use the catalyst in the fluidized bed reactor, it was ground (Retsch SM 2000) and sieved to 0.4–0.8 mm. The surface characteristics of the catalyst were determined by N<sub>2</sub> adsorption-desorption (Micromeritics ASAP 2010), and the isotherm obtained was reported elsewhere [28]. The catalyst has a low BET surface area of 19 m<sup>2</sup> g<sup>-1</sup>, a pore volume of 0.04 cm<sup>3</sup> g<sup>-1</sup> and an average pore diameter of 122 Å.

The temperature programmed reduction (TPR) of the catalyst was performed in an AutoChem II 2920 Micromeritics and reported in a previous paper [28]. A main peak in the TPR curve was observed at 550 °C associated with NiO reduction interacting with α-Al<sub>2</sub>O<sub>3</sub>. Besides, another peak was observed at 700 °C, which, according to the composition given by the supplier, is associated with NiAl<sub>2</sub>O<sub>4</sub> reduction. Prior use the catalyst was subjected to an in situ reduction at 710 °C for 4 h in a 10% vol. H<sub>2</sub> stream.

Moreover, the coke in the spent catalyst was characterized by means of temperature programmed oxidation (TPO) in a Thermo Scientific TGA Q5000TA IR coupled in-line with a Balzer Instruments Thermostat mass spectrometer in order to follow the formation of coke oxidation

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