



# Hydrogen-rich gas production by continuous pyrolysis and in-line catalytic reforming of pine wood waste and HDPE mixtures



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## ABSTRACT

The continuous pyrolysis-reforming of pine sawdust and high density polyethylene mixtures (25, 50 and 75 wt% HDPE) has been performed in a two-stage reaction system provided with a conical spouted bed reactor (CSBR) and a fluidized bed reactor. The influence HDPE co-feeding has on the conversion, yields and composition of the reforming outlet stream and catalyst deactivation has been studied at a reforming temperature of 700 °C, with a space time of 16.7 g<sub>cat</sub> min g<sub>feeding</sub><sup>-1</sup> and a steam/(biomass + HDPE) mass ratio of 4, and a comparison has been made between these results and those recorded by feeding pine sawdust and HDPE separately. Co-feeding plastics enhances the hydrogen production, which increases from 10.9 g of H<sub>2</sub> per 100 g of feed (only pine sawdust in the feed) to 37.3 g of H<sub>2</sub> per 100 g of feed (only HDPE in the feed). Catalyst deactivation by coke is attenuated when HDPE is co-fed due to the lower content of oxygenated compounds in the reaction environment. The higher yield of hydrogen achieved with this two-step (pyrolysis-reforming) strategy, its ability to jointly valorise biomass and plastic mixtures and the lower temperatures required compared to gasification make this promising process for producing H<sub>2</sub> from renewable raw materials and wastes.

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## 1. Introduction

The environmental awareness associated with the use of traditional resources (natural gas, petroleum and coal) has promoted the development of new routes for sustainable hydrogen production, whose demand is increasing because of its interest as an energy carrier and reactant in hydroprocessing units in refineries [1]. Within this scenario, biomass plays an important role as an alternative feedstock, given that it is a CO<sub>2</sub> neutral renewable source, and therefore allows producing sustainable chemicals and fuels [2].

Amongst the different thermochemical routes, direct steam gasification [3–5] and the indirect route of bio-oil reforming [6–9] are the ones most studied for hydrogen production from biomass. The aim of gasification is to produce syngas, with tar formation being an issue for further industrial applications [10,11]. The indirect route of bio-oil reforming has several problems related to its properties and its vaporization and re-polymerization [12,13]. Accordingly, the two-stage strategy made up of pyrolysis and steam reforming has been gaining increasing attention in recent years because it avoids the need for condensing the pyroly-

sis outlet stream and re-vaporizing the bio-oil to be fed into the reforming reactor [14–18]. This process, in which each step is carried out in a different reactor, has its advantages over the single-step process of pyrolysis and in-situ reforming. On the one hand, the temperature in each step can be optimized in order to maximize the production of hydrogen [19] and, on the other hand, the catalyst is more effective for volatile transformation, i.e., the process is more versatile for establishing the desired catalyst/feed ratio. Therefore, a more uniform product stream will be obtained because the catalyst is more efficient at attenuating secondary reactions.

Nevertheless, the biomass feedstock's low hydrogen content and high oxygen content are a drawback for high hydrogen production. Moreover, the catalyst undergoes a considerable deactivation by coke [16]. Consequently, the objective of this study is to increase H<sub>2</sub> production and attenuate catalyst deactivation by jointly valorising biomass and HDPE mixtures.

Several authors report hydrogen production increases by gasifying biomass with HDPE [20–23]. Furthermore, co-feeding overcomes the seasonal limitations of biomass availability and helps to mitigate the environmental problems associated with waste plastic management. Although pyrolysis is considered a suitable route for the large-scale valorisation of waste plastics, and particularly polyolefins [24–27], studies involving pyrolysis and in-line

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catalytic steam reforming of biomass–plastic mixtures are very scarce. Alvarez et al. [19] have studied the co-feeding of polypropylene in the pyrolysis–reforming of biomass in a batch laboratory scale reactor, obtaining higher gas yields and higher hydrogen productions than those with only biomass in the feed. In the same experimental unit, Kumagai et al. [28] performed the pyrolysis–reforming of a biomass/polypropylene mixture on a Ni–Mg–Al–Ca catalyst synthesized by co-precipitation, obtaining a maximum hydrogen production of 6.0 g of H<sub>2</sub> per 100 g of feed when the catalyst was calcined at 500 °C.

The aim of this study is to increase hydrogen production by co-feeding plastics into a continuous two-step process. Moreover, the influence of their joint valorisation on process performance and catalyst deactivation was analyzed. The novel strategy proposed combines the good performance of the CSBR for the pyrolysis of biomass [29] and plastics [30] with the suitability of the fluidized bed for the catalytic reforming process [31,32]. The vigorous cyclic movement of the sawdust and sand particles coated with melted plastic in the CSBR minimizes segregation problems and avoids bed defluidization. Furthermore, the fluidized bed catalytic reactor allows controlling the temperature of the endothermic reforming reaction and delays the blocking of the bed by coke formation. This two-step configuration has been described in previous papers for the pyrolysis–reforming of biomass [16] and plastics [33], reporting a good performance of the process with high hydrogen yields and without operational problems.

## 2. Materials and methods

### 2.1. Materials

Pine sawdust (*pinus insignis*) waste has been milled and sieved to a particle diameter in the 1–2 mm range, which is a suitable particle size for guaranteeing the good performance of the solid feeding system. It was then dried to a moisture value of around 10 wt%. The HDPE provided by Dow Chemical in the form of chippings (4 mm) has the following properties: average molecular weight, 46.2 kg mol<sup>-1</sup>; polydispersity, 2.89 and density, 940 kg m<sup>-3</sup>. The higher heating values (HHV) of both feedstocks are reported in Table 1, together with the results of ultimate and proximate analyses, which have been determined using the equipment described in previous studies [29].

A commercial Ni reforming catalyst (G90-LDP) provided by Süd Chemie (Germany) has been used for the reforming step. The original catalyst (in the form of 10 hole rings, 19 × 16 mm) has been milled and sieved to a particle size in the 0.4–0.8 mm range to guarantee suitable fluid-dynamic conditions in the fluidized bed. The metal content (provided by the supplier) and physical properties (measured by N<sub>2</sub> adsorption–desorption) of the catalyst are

summarized in Table 2. As observed, the catalyst has low BET surface area and porosity.

The catalyst has been reduced in-situ in order to ensure its activity. Thus, based on the results obtained by temperature programmed reduction, it has been reduced for 4 h under 10 vol% H<sub>2</sub> at 710 °C. Both the adsorption–desorption isotherms and the TPR profile of this catalyst are detailed elsewhere [34,35].

### 2.2. Equipment and reactors

Fig. 1 shows the experimental equipment used for the pyrolysis–reforming process. The unit is equipped with two in-line reactors: (i) a CSBR for the pyrolysis of biomass and HDPE mixtures and (ii) a fluidized bed for the subsequent reforming of pyrolysis volatiles.

The unit is provided with two independent feeders for biomass and HDPE in order to avoid the segregation observed when both materials were mixed in a single feeder. The biomass and HDPE are loaded into the dispenser on each feeder from the top of the feeding system. As the piston rises, the entire system vibrates, and the feed is discharged through a water-cooled pipe that connects the feeders with the CSBR. In addition, steam condensation in the vessel is avoided by feeding a small flow of N<sub>2</sub> from the top of the feeding system.

A pump (Gilson 307) has been used to supply the reactor with water, which has been vaporized by a heating cartridge before entering the gas preheater. N<sub>2</sub>, H<sub>2</sub> and air can also be fed into the CSBR, with their flows being controlled by mass flow controllers, which allow feeding up to 20 L min<sup>-1</sup> of nitrogen and air, and up to 5 L min<sup>-1</sup> of hydrogen. The temperature of the steam and gases (pyrolysis inlet stream) is increased to that of the pyrolysis process in a gas preheater packed with stainless steel pipes that is located in the lower section of the pyrolysis reactor.

The pyrolysis step has been performed in a CSBR. This reactor has been successfully used in the pyrolysis and gasification of different waste materials, such as biomass [4,36], plastics [37,38] and tyres [39,40]. The detailed design and main dimensions of the CSBR have been reported elsewhere [16,33]. Reactor temperature is controlled by two thermocouples placed in the annular zone and wall of the CSBR. Before the products are fed into the reforming reactor, they circulate through a cyclone in order to retain sand fines and the char particles entrained from the CSBR.

In order to avoid bed plugging due to coke deposition, which has been observed in a fixed bed reactor [34], a fluidized bed has been used for the reforming of pyrolysis volatiles, whose dimensions are 38.1 mm in diameter and 440 mm in length. The thermocouple located inside the catalyst bed controls the temperature of the fluidized bed reactor. The volatiles from the fluidized bed circulate through a sintered steel filter (5 μm) to retain catalyst fines elutriated from the fluidized bed, with this amount being below 5% of the catalyst bed used in the runs. All the interconnection pipes, high-efficiency cyclone, filter and both reactors are placed inside an oven kept at 270 °C, which ensures that the steam and products are not condensed in the connections between the reactors.

Finally, the condensation system of the plant, consisting of a condenser and a coalescence filter, ensures the full condensation and retention of the products derived from the biomass and HDPE, as well as the non-reacted steam.

### 2.3. Experimental conditions

The attainment of a suitable hydrodynamic performance in the two in-line reactors (the first reactor outlet stream is the second reactor inlet stream) conditions the steam flow rate to feed into the CSBR and the particle size of the sand in it, as well as the par-

**Table 1**  
Pine sawdust and HDPE characterization.

	Biomass	HDPE
Ultimate analysis (wt%)		
Carbon	49.33	85.71
Hydrogen	6.06	14.29
Nitrogen	0.04	0
Oxygen	44.57	0
Proximate analysis (wt%)		
Volatile matter	73.4	99.7
Fixed carbon	16.7	0.3
Ash	0.5	–
Moisture	9.4	–
HHV (MJ kg <sup>-1</sup> )	19.8	43.1

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