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Full Length Article

Role of operating conditions in the catalyst deactivation in the in-line steam reforming of volatiles from biomass fast pyrolysis

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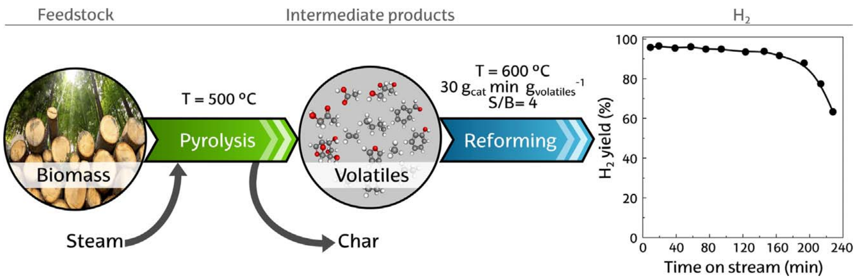
GRAPHICAL ABSTRACT



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ABSTRACT

The effect of reforming conditions (temperature, space time and steam/biomass ratio (S/B)) has been studied in the continuous biomass pyrolysis and in-line catalytic steam reforming process in order to establish suitable conditions for attenuating the deactivation of a commercial Ni catalyst by coke deposition. The experiments have been performed in a conical spouted bed and a fluidized bed reactor for the pyrolysis and reforming steps, respectively. Biomass fast pyrolysis was performed at 500 °C and the reforming operating conditions studied are as follows: 550–700 °C; space time, 10–30 g_{cat} min $g_{volatiles}{}^{-1}$, and; S/B ratio, 2–5. The coke deposited on the catalyst has been analyzed by temperature programmed oxidation (TPO), and two types of coke have been identified, i.e., the coke deposited on the Ni active sites and the one separated from these sites, without filamentous coke being observed by transmission electron microscopy (TEM). Coke deposition has been related to the decomposition of the oxygenates derived from biomass pyrolysis and the re-polymerization of phenolic oxygenates. Suitable conditions to achieve almost full conversion with a H_2 yield of up to 95% and stability for 160 min on stream, are as follows: 600 °C, space time of 30 g_{cat} min $g_{volatiles}{}^{-1}$ and S/B ratio of 3.

1. Introduction

Renewable fuels have attracted significant interest over the last years due to the environmental problems related to the massive use of petroleum based fuels, such as global warming and climate change [1]. In this scenario, biomass is considered one of the most important renewable raw materials with virtually no net contribution to global greenhouse gas [2]. Thermochemical routes (such as gasification and fast pyrolysis) are regarded as the best strategies in terms of their scalability for conversion of biomass into bio-fuels [3]. High bio-oil yields can be obtained at moderate temperatures (around 500 °C) from different types of biomasses and in a delocalized way by using simple design fast pyrolysis technologies [4,5].

Amongst the different alternatives for bio-oil valorization, steam

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reforming has received increasing attention for sustainable H_2 production [6–8]. The main interest of this process lies in its contribution to attenuating the current CO_2 emissions (produced from CH_4 reforming). Moreover, the bio-oil dehydration step, which is required for its valorization as fuel, is not needed for reforming. There are a considerable number of studies dealing with bio-oil reforming and the evolution of reaction indices with time on stream [9–11]. Remón et al. [8] studied the reforming of different bio-oils and reported full carbon conversion in the reforming of pine bio-oil at zero time on stream, and a decrease to 40% in 120 min on stream. The effect of temperature on conversion was also studied in the 500–800 °C range by Remiro et al. [12], who obtained full conversion for 5 h above 700 °C. Nevertheless, several challenges should be faced to avoid bio-oil handling problems in the reforming process [13,14]. Thus, in order to avoid these problems and those related to bio-oil storage, the capability of pyrolysis-reforming of biomass for H_2 production has been recently proven by several authors [15–18] by combining two in-line reactors for biomass fast pyrolysis and the subsequent reforming of volatiles, which allow obtaining a H_2-rich gaseous product.

In previous papers, the good behaviour of the pyrolysis-reforming process by means of a conical spouted bed reactor (CSBR) and an in-line fluidized bed reactor (FBR) has been verified for different feeds, such as biomass [17], high density polyethylene (HDPE) [19], polystyrene (PS) [20] and biomass/HDPE mixtures [21]. In these studies, the performance of the CSBR is proven for pyrolysis of irregular texture or/and sticky materials, specifically for biomass [22–24]. Besides, the FBR is a suitable reactor for reforming, as it allows attaining a homogeneous temperature and attenuating operational problems reported in the literature for fixed bed reactors due to the high amount of coke deposited on the catalyst [25].

Nevertheless, the deactivation of the catalyst is a determining factor for its selection, reactor design, establishment of the optimum operating strategy and viability of pyrolysis-reforming of biomass when scaling up. Although pyrolysis-reforming studies dealing with the characterization of deactivated catalysts are very scarce in the literature, it is well-established that coke deposition is the main deactivation cause of Ni based catalysts [26–29]. The deactivation rate is a consequence of coke formation and gasification rates, which are influenced by reaction conditions [12,30]. In order to improve catalyst activity and stability, different metal phases and promoters have been investigated in the reforming of bio-oil [31–33]. Rioche et al. [34] used a 1% $Pt/CeZrO_2$ catalyst and obtained low catalyst deactivation after 9 h on stream. Valle et al. [35] obtained higher stability of a $Ni/\alpha\text{-}Al_2O_3$ catalyst by adding La_2O_3 as promoter. Fu et al. [36] also reported higher stability of a $Ni\text{-}Ce/Al_2O_3$ catalyst up to 6 h on stream.

The aim of this study is to investigate the effect reforming temperature, space time and steam/biomass (S/B) ratio have on the reforming products, and especially on catalyst deactivation, with the objective of establishing suitable conditions for attenuating this problem. Accordingly, an original continuous two-step pyrolysis-reforming process has been developed, which is a novel alternative to the indirect bio-oil reforming strategy and avoids the operational problems related to bio-oil handling. In addition, the pyrolysis-reforming process allows for treating the whole biomass derived volatile stream, including bio-oil and gaseous products, which involves a remarkable advantage compared to the bio-oil reforming process. Thus, the mentioned different composition of the stream fed into the reforming step in the in-line pyrolysis-reforming strategy justifies a detailed investigation on the influence operating conditions have on catalyst deactivation, given that the results obtained for the steam reforming of bio-oil [9–12] are not applicable for this case. Moreover, coke content and type have been determined by temperature programmed oxidation (TPO) and transmission electron microscopy (TEM), in order to understand the role of coke in catalyst deactivation.

Table 1
Properties of the pine wood sawdust used in the study.

Ultimate analysis (wt%)	
Carbon	49.33
Hydrogen	6.06
Nitrogen	0.04
Oxygen	44.57
Proximate analysis (wt%)	
Volatile matter	73.4
Fixed carbon	16.7
Ash	0.5
Moisture	9.4
HHV (MJ kg^{-1})	19.8

2. Experimental

2.1. Materials

Table 1 shows the properties of the pine wood sawdust used in this study (particle size in the 1–2 mm range), which have been determined by ultimate and proximate analyses by means of a LECO CHNS-932 elemental analyzer and a TGA Q5000IR thermogravimetric analyzer, respectively. Moreover, a Parr 1356 isoperibolic bomb calorimeter has been used for the measurement of the higher heating value (HHV).

In addition, a commercial catalyst (G90-LDP) for CH_4 reforming has been used in the reforming step of biomass pyrolysis volatiles, which has been supplied by Süd Chemie (Germany) in the form of ribbed-rings having 10 hole ring shape and 19 × 16 mm size. Nevertheless, a particle size between 0.4 and 0.8 mm was required to attain a stable fluidization regime in the FBR, and therefore the catalyst had to be ground and sieved to that particle size. The chemical formulation of the catalyst is based on NiO (nominal content of 14 wt%), $CaAl_2O_4$ and Al_2O_3. The results obtained by N_2 adsorption-desorption technique (Micromeritics ASAP 2010) have been reported in previous studies [25,37] and revealed a low BET surface area of the catalyst (19 $m^2\,g^{-1}$) and an average pore diameter of 122 Å.

Moreover, the catalyst has been reduced in-situ by feeding a 10 vol% H_2 at 710 °C for 4 h. The reduction temperature was determined by the results obtained in an AutoChem II 2920 Micromeritics by temperature programmed reduction (TPR), with the results being available in previous papers by the research group [25,37]. Two main peaks were observed at around 550 and 700 °C, which were related to the reduction of NiO and $NiAl_2O_4$ phases, respectively.

2.2. Reaction equipment

The bench scale laboratory plant used for pyrolysis-reforming of biomass is provided with the following elements: pyrolysis reactor (conical spouted bed reactor, CSBR) and catalytic reforming reactor (fluidized bed reactor, FBR). These devices together with all interconnection pipes are located inside a forced convection oven in order to maintain the box temperature at 300 °C and avoid the condensation of heavy compounds upstream and downstream the FBR, which in the latter case is essential to avoid the condensation of volatile products prior to their chromatographic analysis. The overall scheme of the plant is shown in Fig. 1.

The CSBR has been previously used by the research group in the pyrolysis and gasification of biomass [22,24,38], plastics [39–41] and tyres [42,43] and has been designed with the following dimensions: height of the conical section, 73 mm; diameter of the cylindrical section, 60.3 mm, angle of the conical section, 30°; diameter of the bed bottom, 12.5 mm, and; diameter of the gas inlet, 7.6 mm. Moreover, a gas preheater is located below the CSBR, which consists of a stainless steel cylindrical shell, with 310 mm in height and 27 mm in internal diameter. It is filled with stainless steel pipes that increase the surface area for heat transfer and heat the gases to the reaction temperature.