

Hydrogen Production from Biomass Pyrolysis and In-line Catalytic Steam Reforming

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Hydrogen production from pyrolysis-catalytic steam reforming of pine sawdust has been investigated using two subsequent reactors: i) a conical spouted bed reactor for biomass pyrolysis at 500 °C, and ii) a fluidized bed reactor for catalytic reforming of volatiles from the pyrolysis step. A commercial Ni reforming catalyst has been used for the reforming step (Reformax® 330). 99.7 % conversion and a H₂ yield of 93.45 % are achieved at 600 °C, 0.28 g_{catalyst} h g_{biomass}⁻¹ and S/C ratio of 8.2, producing 11.2 g of hydrogen per 100 g of biomass fed into the process. Increasing reaction time, higher coke contents are deposited on the catalyst due to secondary reactions. This is the main cause of catalyst activity decrease, although deactivation is attenuated by the good performance of the fluidized bed reactor and the excess of steam in the reaction medium (high S/C ratio).

1. Introduction

Hydrogen is regarded as an alternative energy carrier and has received much attention due to its several advantages, such as near-zero carbon emissions at the point of use (Acar and Dincer, 2014). Moreover, it is a raw material which is widely used for oil refineries and ammonia and methanol production, and nowadays is still mainly produced by reforming of natural gas and oil derived feedstocks (Balat and Kirtay, 2010).

In order to satisfy the growing demand of hydrogen and reduce greenhouse gas emissions to the atmosphere, other alternative routes from renewable sources are becoming essential for the near future. Among the different renewable sources available, biomass is accepted as the best route for hydrogen production in terms of environmental impact criteria, since it does not contribute to a net increase in atmospheric carbon dioxide (Gil et al., 2014).

Gasification and pyrolysis are two effective methods to convert biomass into hydrogen (Alvarez et al., 2014a), although pyrolysis is energetically more efficient due to the lower temperature required for the process. Flash pyrolysis of biomass allows obtaining a gas yield of 10-20 %, bio-oil yield of 60-80 % and char yield of 15-25 %, depending on the type of biomass and reactor used and operating conditions (Amutio et al., 2012). In order to obtain a hydrogen-rich gas, a catalytic steam reforming step is required subsequent to the pyrolysis process. Fixed bed reactors have been extensively used for reforming processes (Bimbela et al., 2013), although some authors have proven that fluidized beds are more suitable. The maximum hydrogen yield obtained by Lan et al. (2010) in a fluidized bed reactor has been 7 % higher than that in a fixed bed.

Catalytic reforming of bio-oil aqueous fraction and catalytic reforming of raw bio-oil have been extensively investigated in the literature. Several modified Ni-Al catalysts have been studied by Yao et al. (2014) for the catalytic reforming of the bio-oil aqueous fraction, obtaining a maximum hydrogen yield of 56.46 % of the stoichiometric one by using a Ni-Mg-Al catalyst. Remiro et al. (2013) studied the steam reforming of the raw bio-oil in a fluidized bed reactor on a Ni/La₂O₃- α -Al₂O₃ catalyst and have obtained a high bio-oil conversion (>80 %) and a maximum hydrogen yield of 95 % of the stoichiometric one in the 600-800 °C range. Ni-based catalysts are the most common catalysts for reforming bio-oil aqueous fraction (Remón et al., 2014), raw bio-

oil (Remiro et al., 2013) or ethanol (Montero et al., 2014), although noble metals, such as Pt, Pd and Rh, can also be used for reforming oxygenated compounds (Rioche et al., 2005).

Nevertheless, studies dealing with the catalytic reforming in-line of biomass pyrolysis volatiles are rather scarce. A two-stage continuous screw-kiln reactor has been used for this process by Efika et al. (2012), obtaining a maximum H₂ production of 44.4 vol. % when a NiO/Al₂O₃ catalyst was used.

In this study, continuous pyrolysis of biomass and in-line catalytic reforming of volatile products has been performed in a two-stage system, using a commercial Ni reforming catalyst in the second step. This process allows valorizing both the whole bio-oil and gases from the pyrolysis step, avoiding additional costs and bio-oil vaporization operational problems that occur during the bio-oil reforming process in one step. The aim of the work is to ensure the good performance of the two-stage system and study the product distribution obtained and catalyst deactivation.

2. Experimental

2.1 Raw material and catalyst

The raw material used in this study is forest pinewood waste (*Pinus insignis*) with a particle size between 1 and 2 mm and moisture content below 10 %. Its main characteristics are summarized in Table 1.

Table 1: Pinewood sawdust characterization (on a wet basis)

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
Calorific value (MJ/kg)	19.8

The catalyst (Reformax[®] 330) was supplied by Süd Chemie in the shape of perforated rings (19 x 16 mm) and consists of a Ni metal phase supported on Al₂O₃ which is doped with Ca. The chemical formulation of the catalyst is NiO, CaAl₃O₄ and Al₂O₃. The catalyst rings have been crushed and sieved to particles with a diameter of 0.4-0.8 mm and have been reduced by introducing a 10:90 % vol. mixture of H₂ and N₂ at 710 °C for 4 hours.

2.2 Experimental unit and procedure

The experimental equipment used to perform the pyrolysis-catalytic steam reforming of biomass is shown in Figure 1. The system for solid feeding consists of a vessel equipped with a vertical shaft connected to a piston placed below the material bed. The biomass is fed into the reactor by raising the piston at the same time as the whole system is vibrated by an electric engine. The tube that connects the feeding system with the reactor is cooled with tap water and, in order to avoid the condensation of steam in the feeding system, a small nitrogen flow is introduced from the top of the feeding vessel. Water has been fed by means of a Gilson 307 pump and vaporized by an electric cartridge. Other gases, such as nitrogen, air or hydrogen, can also be introduced from the bottom of the pyrolysis reactor, and their flows are controlled by mass flow controllers. Prior to entering the reactor, a gas preheater raises the gases and steam temperature to the reaction temperature.

The main element of the pilot plant is a conical spouted bed reactor where the pyrolysis of biomass has been carried out. This reactor has been designed with the knowledge acquired in the pyrolysis of different waste materials, such as tyres (Lopez et al., 2009), plastics (Artetxe et al., 2010) and different types of biomass like pine sawdust (Amutio et al., 2012) or rice husk (Alvarez et al., 2014b). The volatile products leave the reactor and pass through a high-efficiency cyclone in order to remove the char particles.

The reforming step has been carried out in a fluidized bed reactor. The gases leaving the reactor circulate through a volatile condensation system consisting of a condenser and a coalescence filter. The condenser is a double shell tube cooled by tap water and the coalescence filter removes completely the liquid from the gaseous stream.

The volatile stream has been analysed on-line by means of a GC (Agilent 6890). The sample has been injected into a GC through a line thermostated at 280 °C in order to avoid the condensation of heavy oxygenated compounds. Moreover, the non-condensable gases have been analysed in a micro GC (Varian 4900).

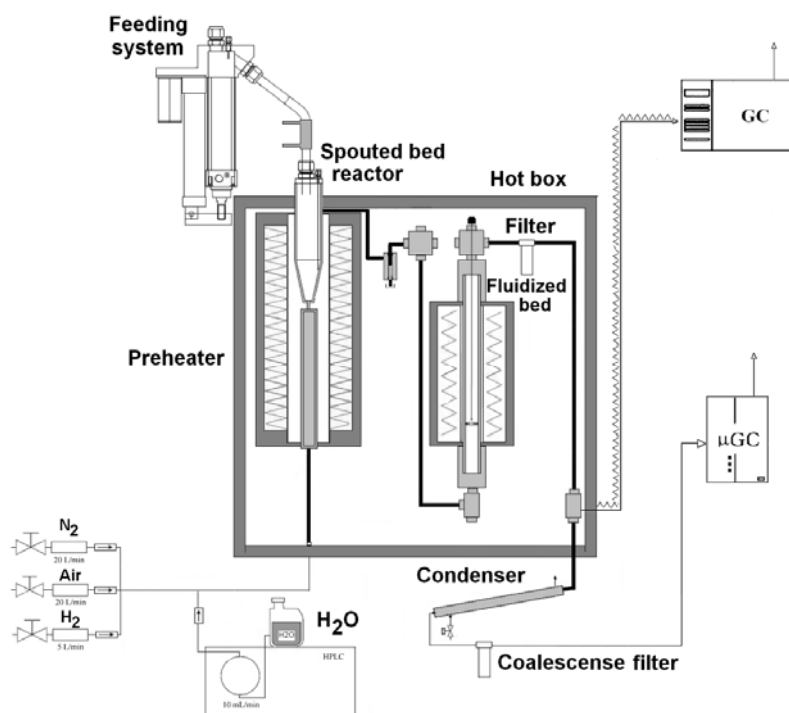


Figure 1: Scheme of the pyrolysis-catalytic steam reforming unit

The biomass and steam have been continuously fed into the reactor with rates of 0.75 g min^{-1} and 3 mL min^{-1} , respectively, corresponding to a steam/biomass ratio of 4 ($S/C=8.2$). The pyrolysis step has been carried out at $500 \text{ }^\circ\text{C}$ and the bed was made up of 50 g of sand with a particle diameter in the $0.3\text{-}0.355 \text{ mm}$ range in order to guarantee a vigorous movement and bed isothermicity. The reforming step has been carried out at $600 \text{ }^\circ\text{C}$ and with a space-time of $0.28 \text{ g}_{\text{catalyst}} \text{ h g}_{\text{biomass}}^{-1}$, using 12.5 g of catalyst (particle diameter in the $0.4\text{-}0.8 \text{ mm}$ range) and 12.5 g of sand (particle diameter in the $0.3\text{-}0.355 \text{ mm}$ range).

3. Results

3.1 Reforming indices

In order to quantify the products of the reforming process, conversion and product yields have been defined as reaction indices. The conversion is calculated as the ratio of molar flow of C from the biomass pyrolysis volatiles converted to the gas fraction in the reforming step (Eq (1)).

$$X = \frac{\text{molar flow of C in the gas fraction}}{\text{molar flow of C in the feed}} \times 100 \quad (1)$$

Moreover, hydrogen yield is calculated as percentage of the maximum allowed by stoichiometry (Eq (2)) and the yields of CO , CO_2 , CH_4 and light HCs (ethylene, ethane, propylene, propane) are calculated as the ratio between the molar flow of C in each one of these components and the molar flow of C in the feed (Eq (3)).

$$Y_{\text{H}_2} = \frac{\text{molar flow of H}_2 \text{ obtained}}{\text{maximum allowed by stoichiometry}} \times 100 \quad (2)$$

$$Y_i = \frac{\text{molar flow of C in } i (\text{CO}_2, \text{CO}, \text{CO}_4, \text{HCs}) \text{ obtained}}{\text{molar flow of C in the feed}} \times 100 \quad (3)$$

3.2 Catalytic steam reforming of volatiles from biomass pyrolysis

Firstly, the limited reactivity steam has at low temperatures (500 °C) has been proven in the pyrolysis step, i.e., the yields for the different product fractions are similar to those obtained by Amutio et al. (2012) in a previous paper in which nitrogen was used as fluidizing agent. A gas yield of 7.33 %, bio-oil yield of 75.33 % and char yield of 17.34 % have been obtained at 500 °C. The gas is mainly composed of carbon monoxide and carbon dioxide and water is the main compound in the liquid fraction (33.7 %). Among the various types of oxygenated compounds in the bio-oil, phenols are the main products, which are formed in the decomposition of lignin macromolecules above 350 °C (Alvarez et al., 2014b).

Table 2 shows the conversion, the initial product yields and the initial gas composition obtained in the reforming step. As observed, almost all volatiles are reformed into gases and a hydrogen yield of 93.45 % of the stoichiometric one is achieved under the conditions studied. The high conversion obtained evidences the good performance of the conical spouted bed and fluidized bed reactors (high heat and mass transfer rates). Therefore, the two-step system has proven to be suitable for pyrolysis-catalytic steam reforming of biomass, obtaining 11.2 g of hydrogen per 100 g of biomass fed into the process. Full conversion and similar hydrogen yield (95 %) have been obtained by Remiro et al. (2013) in the steam reforming of the raw bio-oil at 700 °C, with $0.14 \text{ g}_{\text{catalyst}} \text{ h g}_{\text{bio-oil}}^{-1}$ (Ni/La₂O₃- α -Al₂O₃) and a S/C ratio of 9 with prior separation of pyrolytic lignin.

Table 2: Results of conversion (%), product yields (%) and gas composition (% vol.) at zero time on stream. Reforming conditions: $T=600 \text{ }^\circ\text{C}$, $\text{space-time}= 0.28 \text{ g}_{\text{catalyst}} \text{ h g}_{\text{biomass}}^{-1}$, $S/C=8.2$

X (%)	99.72
Yields (%)	
Y _{H₂}	93.45
Y _{CO₂}	88.55
Y _{CO}	10.58
Y _{CH₄}	0.56
Y _{H_Cs}	0.04
Gas composition (% vol.)	
H ₂	66.06
CO ₂	30.15
CO	3.60
CH ₄	0.19
H _C s	0.01

Figure 2 shows the evolution of conversion with time on stream. It is noteworthy that catalyst deactivation is only significant for times on stream longer than 60 min, with the decrease in activity being pronounced subsequent to 75 min. The deactivation is due to blocking of active centres by carbon deposition, which has been partially gasified favoured by the reactor hydrodynamics and operating conditions (high S/C ratio). Lan et al. (2010) have proven that carbon deposition in fluidized beds is lower than in fixed beds at the same reaction temperature.

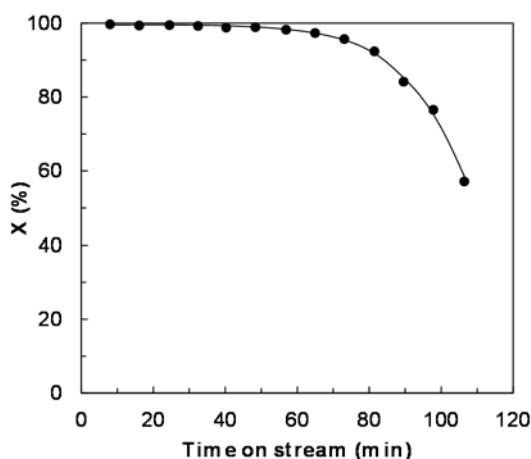


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Regarding gas composition, it is mainly composed of H₂ and CO₂ (reforming products) and small amounts of CO, CH₄ and light HCs (Table 2). Similar values of H₂ concentration have been obtained by Hou et al. (2009) and Seyedejn-Azad et al. (2012) in the reforming of raw bio-oil. In addition, gas composition is slightly affected by coke formation on the catalyst, as shown in Figure 3. H₂ concentration decreases slightly from 66.06 % to 63.51 % after 106 min time on stream due to the decrease in the activity of the catalyst for reforming (Eq (4)) and WGS reactions (Eq (5)), whereas there is no significant change in CO₂ concentration (around 30 %).



When the catalyst is severely deactivated, the cracking reactions of oxygenated compounds become more significant, increasing CO, CH₄ and light hydrocarbon (ethylene, ethane, propylene and propane) concentrations. CO concentration increases from 3.60 % at zero time on stream to 4.93 % at around 106 min, while CH₄ concentration increases from 0.19 % to 0.64 %. Even when the catalyst is deactivated, light hydrocarbon concentration does not exceed 0.13 %. Ethylene is the major compound, followed by ethane and propylene. Propane concentration is negligible throughout 106 min time on stream (<0.01 %). A similar trend has been observed by Remiro et al. (2013) in the reforming of raw bio-oil, obtaining higher yields of CO, CH₄ and light hydrocarbons when the catalyst is deactivated.

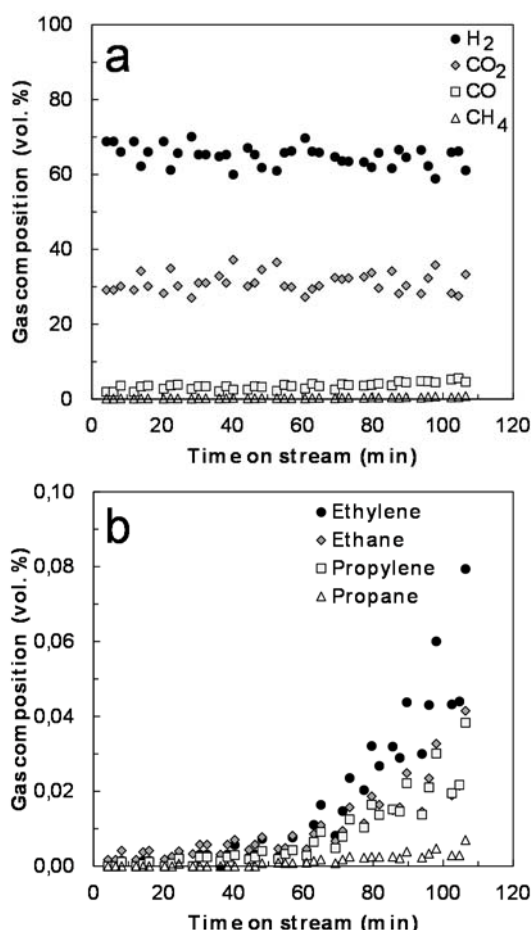


Figure 3: Evolution of gas composition (vol. %) with time on stream: a) H₂, CO₂, CO, CH₄ and b) ethylene, ethane, propylene, propane. Reforming conditions: T=600 °C, space-time= 0.28 g_{catalyst} h g_{biomass}⁻¹, S/C=8.2

4. Conclusions

The two-step reaction system has proven to be suitable for the reforming of volatiles from biomass pyrolysis. The conical spouted bed reactor performs well in the continuous pyrolysis of pine sawdust, given its capacity

for operating in isothermal regime. In addition, the use of a fluidized bed reactor and high S/C ratios in the process helps mitigating coke formation on the catalyst, given that gasification is enhanced under these conditions.

The catalyst has a high activity, which allows a high initial transformation of the volatiles from biomass pyrolysis into H₂ and CO₂ at 600 °C, a space-time of 0.28 g_{catalyst} h g_{biomass}⁻¹ and a S/C ratio of 8.2. The catalyst maintains its activity for 75 minutes and high conversion and hydrogen yield are obtained. After this time on stream, reforming and WGS reactions follow a decreasing trend and secondary reactions take place, producing higher yields of CO, CH₄ and light hydrocarbons.

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