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Hydrogen production by steam reforming of bio-oil/bio-ethanol mixtures in a continuous thermal-catalytic process

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ABSTRACT

The feasibility of the steam reforming of bio-oil aqueous fraction and bio-ethanol mixtures has been studied in a continuous process with two in-line steps: thermal step at 300 °C (for the controlled deposition of pyrolytic lignin during the heating of the bio-oil/bio-ethanol feed) followed by steam reforming in a fluidized bed reactor on a Ni/ α -Al₂O₃ catalyst. The effect of bio-ethanol content in the feed has been analyzed in both the thermal and reforming steps, and the suitable range of operating conditions (temperature and space-time) has been determined for obtaining a high and steady hydrogen yield. Higher ethanol content in the mixture feed improves the reaction indices and reduces coke deposition. Operating conditions of 700 °C and space-times higher than 0.23 g_{catalyst} h (g_{bio-oil+EtOH})⁻¹ are suitable for attaining almost fully conversion of oxygenates (bio-oil and ethanol) and hydrogen yields above 93%, with low catalyst deactivation.

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Introduction

A biomass-based plant (bio-refinery) is the best solution to combine and integrate various processes for converting plant-based biomass to chemicals, energy and materials in order to maximize economic and environmental benefits, while minimizing waste and pollution [1]. Sultana and Kumar [2] found that the delivery cost of a feedstock that combines woody biomass and agricultural biomass is lower than that for a single type of biomass. Consequently, the joint valorization of oxygenated compounds derived from different types of biomasses, such as bio-oil and bio-ethanol (e.g. by catalytic

steam reforming for obtaining H₂), is an interesting route for the development of the bio-refinery concept. Bio-oil is produced by fast pyrolysis of woody biomass, such as mill and harvest residues [3], and bio-ethanol can be sustainably obtained by hydrolysis/fermentation of agricultural lignocellulosic biomass [4,5].

The bio-oil is a complex mixture of water and oxygenated compounds (acids, alcohols, ketones, phenols, furans, etc.), whose composition depends on the biomass source and operating conditions of pyrolysis [6]. The viability of bio-oil reforming process is curtailed by the problems associated with re-polymerization of certain bio-oil components (i.e., derivatives of the lignin contained in biomass) that affect

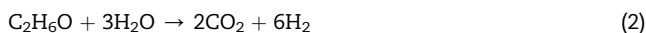
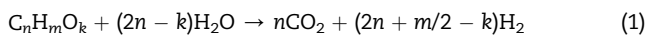
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reactor operation and cause catalyst deactivation. These problems are mitigated with different strategies, such as the valorization of the bio-oil aqueous fraction, the previous separation of pyrolytic lignin and the co-feeding of methanol [7].

The lignocellulosic ethanol has a great potential as a chemical building block for bio-refineries [8] and its catalytic steam reforming avoids the costly dehydration steps required for other valorization strategies. Furthermore, its production cost has been significantly reduced due to advances in the conversion techniques [9].

Besides, bio-ethanol can replace the methanol commonly used to stabilize the bio-oil during its storage [10], which increases the interest of reforming this mixture.

The stoichiometry of the overall reactions for bio-oil and ethanol steam reforming are given by Eqs. (1) and (2), respectively:



In practice, the hydrogen yield is lower than the stoichiometric maximum due to undesired secondary reactions (thermal decomposition of oxygenates, methanation, reverse-WGS reaction, ethanol dehydration or dehydrogenation).

Nickel-based catalysts have been widely used in the literature for reforming the aqueous fraction of bio-oil [11,12] and ethanol [13–15] due to the high C–C bond-breaking activity and the relatively low cost. Among oxide supports, Al₂O₃-based supports are often used as reforming catalysts because of their mechanical and chemical resistance [16].

This paper analyzes the feasibility of the steam reforming of bio-oil aqueous fraction and bio-ethanol mixtures on Ni/ α -Al₂O₃ catalyst in a continuous process with two steps in line (thermal and catalytic) (Fig. 1). This two-step system minimizes the problems inherent to the bio-oil catalytic valorization, caused by the deposition of carbonaceous solid (pyrolytic lignin) during feed preheating [17]. The effect bio-ethanol in the feed has on both the thermal and the reforming steps is analyzed and the suitable range of operating conditions (temperature and space-time) is determined for obtaining steady and high hydrogen yield.

Experimental

Preparation and characterization of bio-oil/bio-ethanol mixtures

Bio-oil was obtained by flash pyrolysis of pine sawdust in a semi-industrial demonstration plant located in Ikerlan-IK4 technology center (Alava, Spain), with a biomass feeding capacity of 25 kg h⁻¹ [18]. The aqueous fraction (82 wt% water) was obtained by phase separation after adding water to the raw bio-oil in a water/bio-oil mass ratio = 2/1 [19]. For every 100 g of raw bio-oil (composed of 65 g of oxygenated compounds and 35 g water) two fractions are obtained: 15 g of organic fraction and 285 g of aqueous fraction. The bio-oil/bio-ethanol mixtures were prepared by adding aqueous ethanol (82 wt% water) to the bio-oil aqueous fraction in mass ratios ranging from 80/20 up to 20/80. In this paper the mixtures are denoted as B_x/E_y, where x is the percentage (wt%) of bio-oil aqueous fraction (B) and y is the percentage (wt%) of aqueous ethanol (E) in the mixture.

The composition of the raw bio-oil, the bio-oil aqueous fraction and the bio-oil/bio-ethanol mixture B₅₀/E₅₀ (Table 1, on a dry basis) was determined by GC/MS analyzer (Shimadzu QP2010S device). Bio-ethanol addition to the bio-oil aqueous fraction only contributes to molecular dilution of the bio-oil oxygenates. The reactivity reported between light alcohols and organic compounds [20] is not observed probably because the mixture is highly diluted in water (82 wt%). The difference between the ethanol content in the mixture B₅₀/E₅₀ (52 wt%) and the nominal content (50 wt%) is caused by cumulative errors in the mixture preparation (a large quantity to conduct all experiments) and by the chromatographic analysis (the compounds with highest molecular weight are not detected).

The elemental composition (C, H, O) of the raw bio-oil, bio-oil aqueous fraction and pyrolytic lignin deposited in the thermal step was determined by elemental analysis (Leco CHN-932 analyzer and ultra-microbalance Sartorius M2P). The resulting molecular formulas (on a dry basis) are C_{4.3}H_{7.2}O_{2.6} and C_{4.1}H_{7.4}O_{2.7}, for the raw bio-oil and bio-oil aqueous fraction, respectively. The water content of (bio-oil aqueous fraction)/bio-ethanol mixtures (82 wt%) was quantified by Karl Fischer titration in a 870 KF Titrino Plus device.

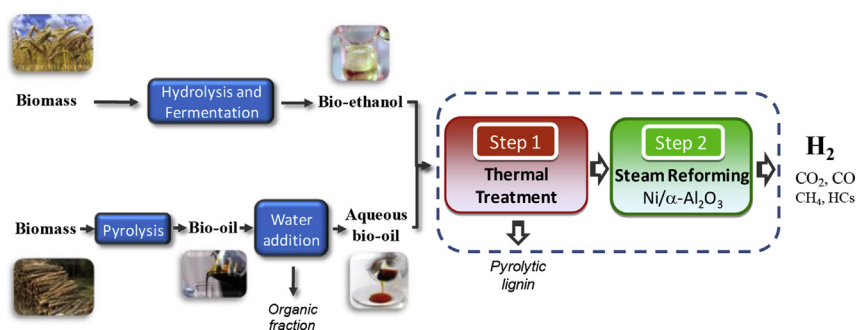


Fig. 1 – Hydrogen production layout according to the joint steam reforming of bio-oil and bio-ethanol obtained from biomass.

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