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Steam reforming of raw bio-oil over Ni/La_2O_3-αAl_2O_3: Influence of temperature on product yields and catalyst deactivation

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ABSTRACT

The hydrogen production by steam reforming (SR) of raw bio-oil (obtained by fast pyrolysis of pine sawdust) has been studied in a continuous two-step process, which consists of a thermal treatment at 500 °C, followed by SR in a fluidized bed reactor with Ni/La_2O_3-αAl_2O_3 catalyst. The effect of SR temperature on bio-oil conversion, product yields and catalyst deactivation was evaluated in the 550–700 °C range. The bio-oil conversion and H_2 yield were significantly enhanced by increasing temperature. A H_2 yield of around 88% and low catalyst deactivation were achieved at temperatures above 650 °C, for a S/C (steam/carbon) ratio of 6 and space-time of 0.10 $g_{catalyst}h/g_{bio\text{-}oil}$. The influence temperature has on product yields and catalyst deactivation was explained by the different nature of the coke deposited. The temperature-programmed oxidation (TPO) curves of coke combustion allow identifying two fractions: i) *Coke I*, which is the main responsible for deactivation (by encapsulating the Ni sites), whose formation depends on the concentration of bio-oil oxygenates; ii) *Coke II*, which has filamentous nature and CO and CH_4 as main precursors. The effect of temperature on the formation of both types of coke depends on the space–time. Thus, for low values (0.04 $g_{catalyst}h/g_{bio\text{-}oil}$) there is significant formation of both types of coke, with their content increasing with temperature. For higher values (0.38 $g_{catalyst}h/g_{bio\text{-}oil}$), the increase in reaction temperature promotes the removal of *coke I*, and therefore this is the prevailing fraction at 550 °C and is negligible at 700 °C. This fact is of special relevance for attenuating the Ni/La_2O_3-αAl_2O_3 catalyst deactivation.

1. Introduction

The growing trend of global energy demand determines the energy transition in the forthcoming decades, which is always subjected to economic viability and environmental impact. In this context, it is clearly essential to develop technologies that maximize the use of energy from renewable sources, which have the potential to provide up to 3000 times the current global energy demand [1]. In the transition from current situation towards a sustainable energy system, the lignocellulosic biomass is an important emerging resource with an undeniable interest for obtaining H_2, because of its nature of renewable source, universal availability, and "zero" net generation of CO_2 [2]. The advantages of fast pyrolysis for obtaining bio-oil, with simple, versatile and globally widespread technologies [3,4], make this liquid product an interesting vector for the large-scale production of H_2 by steam reforming (SR) [5].

The studies on raw bio-oil SR have been hampered by its instability, due to the presence of certain oxygenates (especially the phenolic compounds derived from biomass lignin), whose polymerization during bio-oil heating causes operating problems in the reactor (plugging the feeding system, and even the gas pipelines) and in catalyst deactivation [6]. Consequently, most of the works have been focused on the SR of bio-oil model compounds and bio-oil aqueous fraction, whereas papers that study the SR of raw bio-oil are very scarce [5,7]. The reforming studies of model oxygenates (acetic acid, ethanol, phenol, acetol, etc.) have allowed gaining knowledge of the fundamentals of bio-oil reforming (such as the behavior of different catalysts based on Ni and noble metals).

Coke deposition is the main cause of catalyst deactivation in the SR processes of hydrocarbons and oxygenated compounds, for which different types of coke (pyrolytic, encapsulating and filamentous) have been distinguished. Each coke fraction is formed from different precursors and have different influence on catalyst deactivation, and therefore on H_2 and byproduct yields [8–11]. In these processes, the first stage in coke formation mechanism is considered to be the adsorption of monoatomic carbon on the metal sites, which can polymerize and encapsulate these active sites, thus being responsible for rapid deactivation [12–15]. The filamentous coke formation is caused

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by the dissolution of C atoms on the metal sites, leading to the formation of carbides (e.g., NiC), and further diffusion towards support where preferential precipitation occurs. Consequently, the carbon filaments grow outwards the catalyst particles, thus separating the metal sites from support [9]. In the ethanol steam reforming, CO and CH_4 have found to be the main precursors of this filamentous coke, by reactions of Boudouard ($2CO \leftrightarrow C + CO_2$) and decomposition ($CH_4 \rightarrow 2H_2 + C$) [13–15]. This type of coke is usually not related to significant loss of catalyst activity [16], unless large amount of filaments is formed, which may block the access of reactants, may cause fragmentation of catalyst particles, and also loss of active metal during regeneration of the catalyst [17,18]. Therefore, catalyst deactivation in the SR reaction depends more on the morphology and/or location of the coke than on the total amount deposited. In addition, the deactivation rate is determined by the coke formation and gasification reactions, both dependent on the operating temperature [12]. The overall coke formation mechanism is expected to be more complex in the SR of raw bio-oil, since it is a complex mixture of oxygenated compounds with different capacity for reforming and coke formation.

This paper delves into the steam reforming of a raw bio-oil obtained by flash pyrolysis of pine sawdust over Ni/La_2O_3–αAl_2O_3 catalyst. Specifically, the effect of operating temperature on the reaction indices (bio-oil conversion and product yields) obtained with fresh catalyst (at zero time on stream) and also on its deactivation has been analyzed. The objective is to gain more knowledge on the appropriate conditions for the SR process, by using a continuous two-step (thermal-catalytic) reaction system. Given that catalyst deactivation is one of the main constraints of this process, special emphasis has been focused on studying the coke deposited with a view to determining the precursors of its deposition. For this purpose, the total content, nature and/or location of the coke have been related with the deactivation rate, and also with the composition of reaction medium.

Thereby, the results shown below correspond to experimental conditions of rapid catalyst deactivation. Furthermore, given that fluidized bed reactor with catalyst circulation (which would be regenerated in another unit) is the most suitable technology for the SR of raw bio-oil on a large scale, it should be highlighted that fluidized bed reactor was used in this work. Accordingly, the results obtained are meaningful with a view to the scale-up of the process.

2. Experimental

2.1. Reaction equipment and operating conditions

The reaction equipment consists of two reactors in-line (Fig. 1). The first reactor (for thermal treatment of bio-oil at 500 °C) is a U-shaped steel tube which is intended to retain the carbonaceous solid (pyrolytic lignin) formed by re-polymerization of phenolic compounds in bio-oil (Step 1). The raw bio-oil was fed as droplets into the thermal unit at a feeding rate of 0.1 ml/min (controlled by an injection pump *Harvard Apparatus 22*), and the additional water required for setting an S/C ratio was fed by *307 Gilson* pump. The thermally treated bio-oil (i.e., the volatile stream leaving the thermal step) access the catalytic fluidized bed reactor (Step 2 in Fig. 1) where SR reaction over Ni/La_2O_3–αAl_2O_3 catalyst is carried out. The reforming conditions were: thermal step, 500 °C; catalytic SR, 550–700 °C; steam-to-carbon ratio (S/C), 1.5 and 6.0; space-time (W/F_0), 0.04 and 0.38 $g_{catalyst}h/g_{bio\text{-}oil}$, atmospheric pressure.

The good performance and versatility of the two-step reaction system (thermal + catalytic) was previously verified for the catalytic conversion of bio-oil into hydrocarbons [19–21], and for the steam reforming of bio-oil aqueous fraction [22,23], raw bio-oil [24], and bio-oil/ethanol mixtures [25,26]. 500 °C was established as adequate temperature in the thermal step for maximizing the yield of volatile stream. Besides, a pyrolytic lignin (PL) with composition suitable for possible commercial exploitation is obtained at this temperature, which would enable full valorization of raw bio-oil [27]. The PL yield (grams of lignin deposited per grams of raw bio-oil fed) was 5.2 wt% and 4.2 wt% for S/C ratio of 1.5 and 6.0, respectively, and its elemental composition was $C_{7.1}H_{2.8}O_{0.7}$.

The lowest steam-to-carbon ratio used in this paper (S/C = 1.5) corresponds to the feed of raw bio-oil, i.e., the minimum value without feeding additional water. The S/C ratio of 6 is suitable for obtaining a high H_2 yield, with low catalyst deactivation and without excessive energy cost [24].

The isothermicity of the catalytic bed is one of the main advantages of using a fluidized bed reactor for reforming bio-oil [28,29]. Moreover, the catalyst deactivation by coke deposition is attenuated due to the good steam-catalyst contact, which promotes gasification of the coke [30]. In order to attain suitable hydrodynamic conditions, appropriate values of gas flow, catalyst particle size and solid mass in the bed are needed. In this work, a catalyst particle size of 150–250 μm was established as suitable for avoiding internal diffusion limitations [31].

The on-line analysis of the reaction products was carried out continuously with a gas chromatograph (*Agilent Micro GC 3000*) provided with four analytical modules for the analysis of: (1) permanent gases (O_2, H_2, CO, and CH_4) with 5A molecular sieve capillary column; (2) light oxygenates (C_{2-}), CO_2 and water (Plot Q capillary column); (3) C_2-C_4 hydrocarbons, with alumina capillary column; (4) oxygenated compounds (C_{2+}) with *Stabilwax* type column.

2.2. Raw bio-oil

The raw bio-oil was obtained by flash pyrolysis of pine sawdust at 480 °C in a semi-industrial demonstration plant, located in Ikerlan-IK4 Technology Centre (Alava, Spain), with a biomass feeding capacity of 25 kg/h [32], whose design was based on results obtained in a laboratory plant (120 g/h) at the University of the Basque Country [33,34]. The elemental composition was analyzed by using a *Leco CHN-932 analyzer* and ultra-microbalance *Sartorious M2P* and the water content was determined by Karl Ficher valorization (*KF Titrino Plus 870*). Some physico-chemical properties of raw bio-oil (pH, viscosity, density) were also quantified (Table 1). These results are consistent with typical properties of bio-oils obtained by fast pyrolysis: high water content, substantial acidity and relatively high viscosity [35,36].

The content of carbon (C), hydrogen (H), and oxygen (O) in the raw bio-oil is 48.1%, 6.0% and 45.9%, respectively. According to the elemental analysis, molecular formula of this bio-oil can be defined by $C_{4.0}H_{6.0}O_{2.9}$. The contents of C and O are similar to those reported by several authors for bio-oils obtained by fast pyrolysis of different types of biomass (pine sawdust, rice hulls, corn stalks, pine wood, wheat straw) [37–39].

Chromatographic techniques (GC/MS, GCxGC/MS) were used to determine the composition of the raw bio-oil. The device used for GC/MS analyses is a *GC/MS-2010S Shimadzu*, provided with a *BPX-5* column (50 m × 0.22 mm × 0.25 μm). Product identification was accomplished by means of the *NIST 147* library, and the calibration factor for the chromatographic analysis were determined by using pattern mixtures containing the main bio-oil compounds. The GCxGC/MS analysis was performed with a *5975C* Mass Spectrometer (*Agilent Technologies*), coupled to a *GC 7890A* provided with a non-polar *DB-5* column and a polar *TRB-50 HT* column. The chromatographic results of raw bio-oil are depicted in Fig. 2, and the composition of the bio-oil after the thermal step at 500 °C (Step 1, in Fig. 1) is shown in Table 2. It should be pointed out that the identified compounds correspond to around 70 wt% of the bio-oil, given that conventional GC/MS techniques do not allow quantifying heavy oxygenates with molecular weight greater than 320 g/mol [40].

2.3. Reaction indices

Steam reforming (SR) of bio-oil proceeds according to the SR