

Operating Strategies for the Oxidative Steam Reforming (OSR) of Raw Bio-oil in a Continuous Two-step System

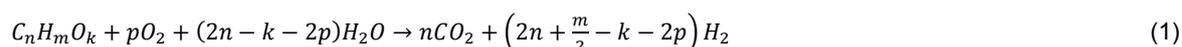
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This work aimed to establish a suitable O_2 feeding strategy for the hydrogen production by oxidative steam reforming (OSR) of raw bio-oil in a reaction system with two-steps: thermal treatment (at 500 °C, for the controlled deposition of pyrolytic lignin) followed by the reforming of the volatile stream in a fluidized bed reactor. Specifically, the effect of co-feeding O_2 before or after the thermal step was analyzed for oxygen-to-carbon molar ratio (O/C) in the 0.34-0.67 range. The catalytic step was kept at 700 °C, steam-to-carbon molar ratio (S/C) = 6.0, and space-time = $0.6 \text{ g}_{\text{catalyst}} \text{ h}(\text{g}_{\text{bio-oil}})^{-1}$. When O_2 is co-fed before the thermal step, there is a partial combustion of both, pyrolytic lignin and oxygenates, thus resulting a lower amount of oxygenated compounds entering the reforming reactor, although the composition of these oxygenates is not affected by the presence of O_2 in the thermal step. As a result, a noticeable lower H_2 yield was obtained when O_2 is fed before the thermal treatment, although catalyst deactivation rate was similar to that obtained when co-feeding O_2 after thermal treatment. Consequently, in the OSR of bio-oil in a two-step system, O_2 must be co-fed after the thermal treatment step; in order to avoid bio-oil oxygenates oxidation prior to the reforming reaction.

1. Introduction

The need for reducing dependence on fossil fuels and minimizing harmful emissions to the atmosphere has boosted the development of sustainable processes for energy and/or chemicals production from renewable resources. Among these, hydrogen production from biomass may play an important role in the future (Dincer & Acar, 2015). The availability of lignocellulosic biomass and the advantages of obtaining a liquid product (bio-oil) by fast pyrolysis with simple, versatile and globally widespread technologies, make the bio-oil an interesting raw material for the sustainable large-scale production of H_2 . The steam reforming (SR) is the process that has received greater attention in the literature for H_2 production from bio-oil (Tanksale et al., 2010; Sarkar & Kumar, 2010; Gollakota et al., 2016). The co-feeding of oxygen (i.e., the oxidative steam reforming, OSR) is an attractive alternative because it promotes oxidation reactions (Harju et al., 2015), whose heat release helps to meet the energy demands of the SR reactions. The energy requirement diminishes with increasing the O_2/C ratio, and there is a ratio that enables the thermo-neutral reaction (auto-thermal reforming, ATR), which is the most energy-efficient process (Vagia & Lemonidou, 2008). The overall OSR reaction of oxygenated species, which also includes the water-gas shift reaction (WGS), is shown in Eq (1):



Furthermore, the addition of O_2 in the SR process could promote the partial combustion of coke precursor compounds, thus decreasing coke deposition on the catalyst (Medrano et al., 2011; Trane et al., 2012). This effect is interesting for the viability of the process, which is conditioned by catalyst deactivation, although it also decreases the potential H_2 yield (Rioche et al., 2005; Czernik & French, 2014).

The reforming of raw bio-oil is hampered by the polymerization in the reactor of some bio-oil components (specially phenolic compounds derived from the pyrolysis of lignin) (Bai et al., 2014), which causes piping blockage in long-operation runs and contributes to a faster catalyst deactivation. In order to overcome these operating problems, a continuous two-step reaction system (thermal+catalytic) was proposed for bio-oil reforming. With this system, a carbonaceous solid (pyrolytic lignin, PL), formed by re-polymerization of bio-oil compounds, is retained in the thermal unit and the resulting volatile stream is reformed in the subsequent

catalytic reactor. The good behavior and versatility of this system was previously verified for catalytic SR of bio-oil aqueous fraction (Valle et al., 2013), of raw bio-oil (Remiro et al., 2013a) and of bio-oil/ethanol mixtures (Remiro et al., 2014).

In this work, this two-step reaction system was used for OSR of raw bio-oil, and two different operating alternatives (co-feeding O₂ before or after the thermal step) were analyzed, in order to establish the strategy that allows the higher and more stable hydrogen production. For this purpose, special attention has been paid to the effect that the combustion of bio-oil components in the thermal step has on catalyst behavior (bio-oil conversion, H₂ yield and stability) in the subsequent catalytic reforming step.

2. Experimental

2.1. Feed and catalyst characteristics

The raw bio-oil was obtained by flash pyrolysis of pine sawdust at 450 °C in a semi-industrial demonstration plant, located in Ikerlan-IK4 Technology Centre (Vitoria, Spain), with a biomass feeding capacity of 25 kg/h. The water content of bio-oil (38 wt %) was determined by Karl Fischer valorization (*KF Titrino Plus 870*), and its elemental composition was analyzed using a *Leco CHN-932* analyzer and ultra-microbalance *Sartorius M2P*. The corresponding molecular formula of bio-oil is C_{4.21}H_{7.14}O_{2.65} (water-free basis). GC/MS technique (*GC/MS-2010S Shimadzu*) was used to identify and quantify the oxygenated composition of bio-oil.

The catalyst (Ni/La₂O₃-αAl₂O₃, denoted NiLaAl) was synthesized by incipient wetness impregnation by using α-Al₂O₃ as support. Prior to Ni loading, the Al₂O₃ support was modified with La₂O₃ by impregnation with an aqueous solution of La(NO₃)₃·6H₂O, under vacuum at 70 °C. The La-modified support was dried at 100 °C for 24 h and calcined at 900 °C for 3 h. Subsequently, Ni was added by impregnation with Ni(NO₃)₂·6H₂O. The nominal contents of Ni and La₂O₃ in the catalyst were 10 wt % and 9 wt %, respectively. After drying 24 h at 110 °C, the final catalyst was calcined at 850 °C for 4 h and it was sieved (150–250 μm). Before each reaction, the catalyst was reduced for 3 h at 850 °C under H₂/N₂ flow (7 % v/v of H₂).

2.2. Reaction equipment, operating conditions, and reaction indices

The continuous reaction equipment consists of two steps in line (Figure 1). The first step (thermal treatment unit, at 500 °C) is a U-shaped steel tube where volatilization of bio-oil and water (co-fed to adjust the desired steam-to-carbon ratio) is carried out, along with deposition of pyrolytic lignin. The bio-oil was fed as droplets entrained by the carrier flow (He) at a feeding rate of 0.08 ml/min and additional water (0.22 ml/min) was fed in order to have S/C ratio of 6. The thermally treated feed (i.e., the volatile stream that leaves this thermal step) is subsequently reformed in a catalytic fluidized bed reactor. The catalytic bed consists of the catalyst (150–250 μm) mixed with an inert solid (CSi carborundum, 37 μm) in catalyst/inert mass ratio > 8, in order to ensure good fluidodynamic conditions and isothermicity of the fluidized bed.

The analysis of the products stream was carried out by gas chromatography (*Agilent MicroGC 490*) and the liquids obtained after condensation of the stream were analyzed by GC/MS (*Shimadzu QP2010S device*). All the experiments were carried out at atmospheric pressure with a small overpressure (0.3–0.4 atm) generated by the products and the carrier gases flow-rates. The OSR conditions were: 700 °C; S/C = 6; space-time, 0.6 g_{catalyst}h/g_{bio-oil}, G_{C1}HSV, 5100 h⁻¹. Figure 1 shows the two operating strategies studied in this work: i) O₂ fed before the thermal step, with O/C ratio of 0.67 (strategy 1), and ii) O₂ fed before the catalytic step, with O/C ratio of 0.34 (strategy 2). These O/C ratios have been selected to ensure working settings close to the autothermal conditions.

Prior to the study of OSR of raw bio-oil in the two-step system, blank runs (without catalyst) were carried out in order to analyze the effect that the presence of O₂ in the thermal step has on the composition of the volatile stream that leaves this unit (i.e., the feed to the catalytic reforming reactor). In these tests the temperature of the fluidized bed reactor (without catalyst) was lower than thermal unit temperature, so that the composition of the stream that leaves the thermal step is not altered.

The bio-oil conversion is quantified from the molar flow-rate (in carbon-units contained) that enters and leaves (un-reacted bio-oil) the catalytic reactor:

$$X_{bio-oil} = \frac{F_{inlet} - F_{outlet}}{F_{inlet}} \quad (2)$$

The H₂ yield is calculated as a percentage of the stoichiometric potential of the feed under SR conditions:

$$Y_{H_2} = \frac{F_{H_2}}{\left(2n + \frac{m}{2} - k\right)F_{inlet}} \quad (3)$$

Where F_{H_2} is the molar flow-rate of H_2 obtained. The yield of carbon-containing products (CO , CO_2 , CH_4 and C_2 - C_4 hydrocarbons) is quantified by:

$$Y_i = \frac{F_i}{F_{inlet}} \quad (4)$$

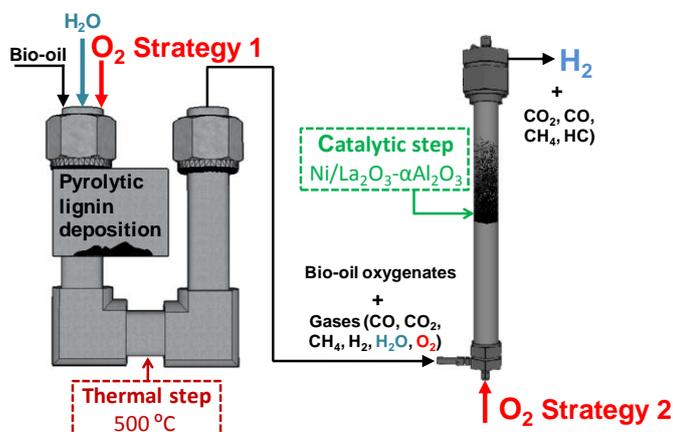


Figure 1: Strategies of feeding O_2 for the OSR of raw bio-oil in the two-steps (thermal-catalytic) continuous equipment.

3. Results and discussion

3.1. Effect of co-feeding O_2 on the volatile stream composition at the thermal step outlet (strategy 1)

Two runs were performed by feeding the bio-oil/water/ O_2 mixture with O/C molar ratio of 0 (corresponding to SR conditions) and O/C of 0.67. The thermal unit was kept at 500 °C, whereas the second unit (without catalyst) was kept at 400 °C, in order to avoid the partial combustion of the volatiles leaving the thermal step, which were analyzed with the previously described GC and GC/MS equipments. The results of bio-oil conversion and gaseous product yields obtained under the different O/C molar ratios are shown in Table 1. Table 2 shows the composition (on a water-free basis) of the liquid, and the composition of the raw bio-oil feed is also shown for comparison.

Table 1: Effect of O/C molar ratio on bio-oil conversion and gaseous product yields in the thermal step (O_2 fed before thermal step, strategy 1).

	O/C=0	O/C=0.67
$X_{\text{bio-oil}}$	0.12	0.52
H_2	0.01	0.01
CO_2	0.05	0.41
CO	0.05	0.10
CH_4	0.01	0.01
C_2 - C_4	0.01	0.02

The results in SR conditions (O/C = 0) indicate that a thermal treatment of bio-oil at 500 °C generates a slightly transformation of oxygenates stream mainly by decarbonylation and decarboxylation reactions (bio-oil conversion \approx 0.12) into CO_2 and CO as main products, with almost negligible amounts of H_2 , CH_4 and C_2 - C_4 hydrocarbons (Table 1). On the contrary, when the O_2 is fed before the thermal step (O/C = 0.67), the bio-oil conversion increases drastically to 0.52 with a CO_2 and CO yields of 0.41 and 0.1 respectively, whereas the rest of products yields (H_2 , CH_4 and C_2 - C_4 hydrocarbons) remain insignificant. This suggests that, in addition to decarbonylation and decarboxylation reactions, the combustion of some oxygenates takes place, thus increasing CO_2 and CO yields. Therefore, it is expected a lower H_2 potential yield in the overall process when the O_2 is fed before the thermal step.

The comparison between the raw bio-oil and treated bio-oil composition (Table 2) shows that the thermal treatment at 500 °C makes a remarkable alteration on treated bio-oil composition, increasing phenols, ketones and levoglucosan amounts, with a lower acids concentration, because in parallel with the decarbonylation and decarboxylation reactions, some oxygenates inter-conversion reactions take place. Nevertheless, the comparison between the 2nd and 3rd column (O/C = 0 and 0.67, respectively) shows that O_2 does not modify

significantly the volatile stream composition after the thermal treatment of bio-oil. This fact suggests that there is no selective combustion of bio-oil oxygenates.

Table 2: Effect of O/C molar ratio on the composition of the liquid fraction of volatile stream at the thermal unit outlet (O_2 fed before thermal step, strategy 1 in Figure 1).

	Raw bio-oil	O/C=0	O/C=0.67
Ketones	22.3	31.8	30.6
<i>acetone</i>	1.1	2.57	3.74
<i>1-hydroxy-2-propanone</i>	15.5	14.33	13.57
Acids	33.3	7.11	5.76
<i>acetic acid</i>	25.3	6.14	4.97
Esters	3.9	5.32	6.98
Aldehydes	8.2	7.17	5.37
Phenols	11.5	19.63	19.1
<i>1,2-benzenediol</i>	2.9	7.18	6.33
<i>phenol</i>	1.1	2.66	2.79
Ethers	0.8	1.33	1.28
Alcohols	1.2	1.59	1.01
Levoglucosan	14.6	20.59	23.46
Others	1.5	2.39	2.91
Not identified	2.7	3.07	3.53

3.2. Effect of co-feeding O_2 on the amount (wt %) of pyrolytic lignin deposited in the thermal step (strategy 1)

The O_2 feeding to the thermal step produces a pronounced decrease in the amount of PL deposited in the thermal step. Thus, a PL deposition of 12 wt % (referred to the bio-oil fed) has been quantified for O/C=0 (without O_2 in the feed) and of 8 wt % for O/C = 0.67, that is, there is ~30 % lower deposition of PL under OSR conditions. This fact may be consequence of: i) the lower total content of compounds precursors of PL formation (which are partially oxidized by O_2) and of ii) partial combustion of the lignin deposited due to the presence of O_2 .

The amount of PL consumed by combustion in the thermal step has been determined by temperature programmed oxidation (TPO) of pyrolytic lignin in a TA Instruments Q5000 IR thermobalance at different O_2 partial pressure, whose effect is shown in the Figure 2. The results reveal a complete combustion of PL when pure air is fed ($P_{O_2} = 0.21$ atm) at 500 °C (thermal step temperature) whereas the combustion rate decreases drastically at $P_{O_2} = 0.04$ atm (corresponding to the OSR runs, O/C = 0.67) removing only a 20 wt % of PL deposited. Therefore, both aforementioned arguments (lower amount of precursor compounds and partial oxidation) contribute to the lower deposition of PL when O_2 is fed to the thermal step (strategy 1).

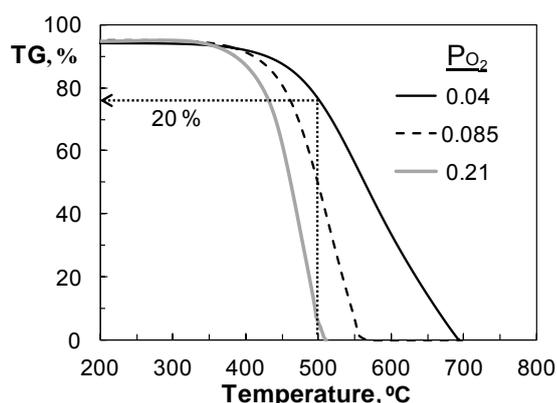


Figure 2: Effect of O_2 partial pressure on pyrolytic lignin combustion.

3.3. Comparison of O_2 co-feeding strategies in the two-steps reaction system

Figure 3 shows the results of the catalytic runs carried out to compare both strategies for O_2 co-feeding proposed in this paper (Figure 1). The results in Figure 3a correspond to the evolution with time on stream of

bio-oil conversion and H₂ and CO₂ yields and Figure 3b shows the yields of CO, CH₄ and light hydrocarbons (C₂-C₄) at the two-steps reaction system outlet in the oxidative steam reforming of bio-oil.

Considering the O₂ uptake in the thermal unit (strategy 1), the corresponding experiment has been carried out with an O/C molar ratio of 0.67, which is double that used when O₂ is directly fed to the reactor (O/C=0.34 in the strategy 2), thus, a similar O/C molar ratio can be achieved in the fluidized bed reactor for both studied strategies.

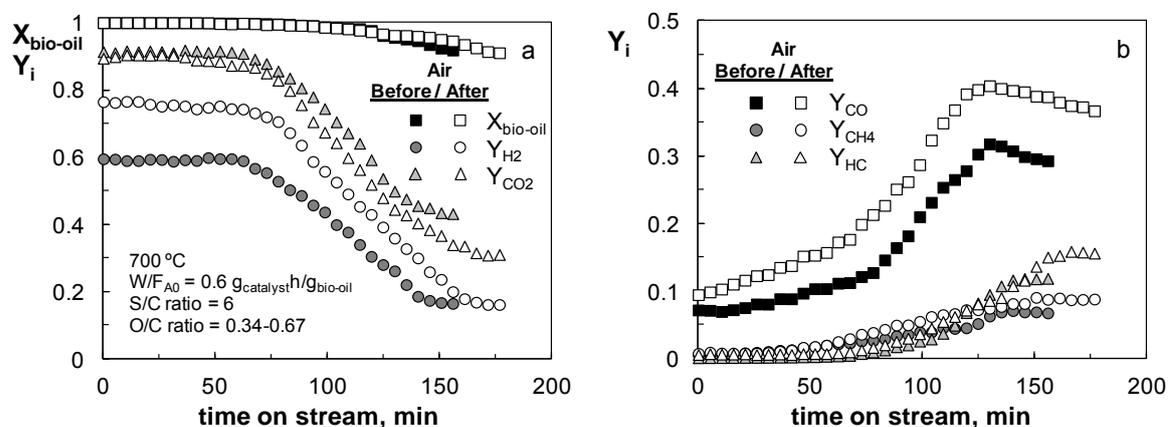


Figure 3: Comparison of the evolution with time on stream of bio-oil conversion and H₂ and CO₂ yields (a) and yields of CO, CH₄ and hydrocarbons (b) for OSR of bio-oil over NiLaAl catalyst when O₂ is fed ($P_{O_2} = 0.04$ atm) before (strategy 1) and after (strategy 2) the thermal step.

Comparing the results at zero time on stream, the highest H₂ yield (76 %) is attained when the O₂ is fed before the catalytic step (strategy 2) (Figure 3a), whereas with strategy 1 setup, the initial H₂ yield is significantly lower (60 %) due to the partial combustion of oxygenates in the thermal treatment of raw bio-oil.

As a consequence of this combustion reaction, the bio-oil conversion and CO₂ yield are similar for both strategies. Even though CO is partially formed by the combustion of some bio-oil oxygenates (Table 1), the slightly lower CO yield at zero time on stream in strategy 1 (Figure 3b), as well as the lower H₂ yield, can be attributed to the lower potential for their formation by reforming reactions, due to a previous partial oxidation of oxygenates in the thermal step. It should be noted that the sum of CO and CO₂ yields achieved in strategy 1 is lower than that achieved in strategy 2, evidencing a lower O₂ consumption despite the O/C molar ratio in strategy 1 is twice that used in strategy 2. A similar behavior is expected for other O/C ratios because unavoidable oxidation reactions always will take place in the thermal step in strategy 1, whilst in the strategy 2, both the reforming and oxidation reactions compete in the catalytic step (with no previous oxygenates oxidation in the thermal step), thus enhancing the H₂ production.

On the other side, the comparison of the yields evolution with time on stream for both strategies shows a pronounced deactivation by coke deposition (Remiro et al, 2013b) after 60 minutes, from which the H₂ and CO₂ yields decrease with time on stream (Figure 3a). The decrease is less noticeable in the strategy 1, as well as the increase with time on stream of CO and CH₄ yields (Figure 3b).

This effect for CO yield can be related to the attenuation of the WGS reaction deactivation (according to the attenuation in the CO₂ yield decrease). Besides, these results indicate a slight delay in the catalyst deactivation by coke deposition when the O₂ is fed before the thermal treatment unit, which can be attributed to the partial oxidation of the bio-oil oxygenates, which are the main precursors of deactivating coke deposition (Remiro et al., 2013b; Aramburu, 2016) and this attenuation it is more noticeable for WGS reaction.

Nevertheless, the deactivation delay achieved with the strategy 1 is minimal, whereas there is a considerable drop in the H₂ yield at zero time on stream. Consequently, for an optimal performance of the two-step reaction system with the Ni/La₂O₃- α Al₂O₃ catalyst, the most suitable strategy is the second one proposed, where the O₂ is fed after the thermal treatment step, avoiding previous oxygenates oxidation.

4. Conclusions

The two-step reaction system allows the raw bio-oil valorization by OSR at 700 °C with an H₂ initial yield of 76 % when the O₂ is fed after the thermal treatment, although the catalyst suffers deactivation by coke deposition.

The strategy where the O₂ is co-fed with bio-oil (prior to the thermal step, strategy 1) produces a slightly favorable effect for attenuating catalyst deactivation, which is related to the combustion of the main precursors of deactivating coke formation. Deactivation attenuation has a higher incidence on the WGS reaction, which contributes to a noteworthy decrease in the CO yield. Nevertheless, the strategy 1 promotes the partial combustion of bio-oil oxygenates, thus lowering reformable compounds entering the catalytic step, and consequently, a lower H₂ yield (60 %) is achieved.

In view of this unfavorable effect, in order to enhance H₂ production by OSR of bio-oil in a two-step reaction system, O₂ must be co-fed after the thermal unit, thus avoiding bio-oil oxygenates oxidation prior to the OSR step.

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