Optimal Conditions of Thermal Treatment Unit for the Steam Reforming of Raw Bio-oil in a Continuous Two-step Reaction System

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The separation of pyrolytic lignin in a previous thermal treatment step is essential for the viability and efficiency of the continuous hydrogen production by steam reforming (SR) of raw bio-oil. This work aimed to establish the conditions of this thermal step that maximize the bio-oil fraction liable to valorization in the subsequent SR reactor, and that lead to a better behavior of the catalyst. The influence that temperature (400-800 °C) and steam-to-carbon ratio S/C (1.5-6.0) have on the composition of resulting volatile stream and on the solid fraction (pyrolytic lignin) deposition was analyzed by feeding raw bio-oil, and a mixture of raw bio-oil and with 20 wt% of ethanol. The thermal treatment temperature affects both the yield of pyrolytic lignin (which decreases with temperature, especially in the range 400-500 °C) and its composition (so that the H/C ratio decreases as the temperature is higher). The yield of liquid fraction and its total content of oxygenates decrease notably above 500 °C. Levoglucosan content decreases, while that of phenols (especially above 650 °C), carboxylic acids (mainly acetic acid) and acetaldehyde increase markedly as temperature is raised. Temperature rise enhances formation of gaseous products (mainly CO and CO_2), with H_2, CH_4 and hydrocarbons being promoted above 600 °C. The effect of thermal step temperature on the Ni/La_2O_3-αAl_2O_3 catalyst behavior was studied by analyzing the evolution with time-on-stream of bio-oil conversion and product yields. Consequently, 500 °C is the thermal treatment temperature that leads to a better compromise between H_2 yield and catalyst stability, since the resulting oxygenated composition causes less deactivation of the reforming Ni/La_2O_3-αAl_2O_3 catalyst, thereby attaining complete and stable bio-oil conversion and H_2 yield close to 90 %.

1. Introduction

The availability of lignocellulosic biomass and the advantages of obtaining bio-oil through simple and highly developed fast pyrolysis technologies (Meier et al., 2013) make the bio-oil a promising renewable raw material. The catalytic steam reforming (SR) of bio-oil, which avoids the costly dehydration steps required for other valorization strategies, is an interesting route for the sustainable production of hydrogen (Chattanathan et al., 2012). However, the direct valorization of raw bio-oil is hampered by its high complexity, corrosivity and thermal instability, which makes the long-term storage problematic, creates plugging problems in the reactor and affects the catalyst deactivation. Several strategies have been proposed in the literature to address these problems, although its satisfactory and scalable solution remains an ongoing challenge. Among the different treatments used are: i) Fractionation by molecular distillation at 80 ºC and 100 Pa (Guo et al., 2010); ii) Treatment at high pressure (200 bar) and moderate temperatures 200-300 ºC (De Miguel Mercader et al., 2010) to reduce oxygen and water content; iii) Dehydration-cracking *in situ* in the pyrolysis reactor, using acid catalysts to reduce the concentration of some compounds, such as methoxy-phenols (Atutxa et al., 2005; Zhang et al., 2009); iv) In-line transformation by dehydration-cracking with HZSM-5 zeolite catalysts of the volatile stream resulting from pyrolysis (French and Czernik, 2010), v) Co-feed with low-cost alcohols (methanol, ethanol, butanol), which causes that reactive carboxylic acids and carbonyl compounds of the bio-oil become their corresponding esters and acetals (esterification) (Moens et al., 2009), thus improving the bio-

oil quality (acidity, viscosity, corrosivity) (Hilten et al., 2014); vi) Thermal treatment at atmospheric pressure, which reduces the concentration of phenols and high molecular weight compounds, which undergo repolymerization that lead to the formation of a solid (pyrolytic lignin) (Bertero et al., 2011); vii) In line retention of pyrolytic lignin in a thermal treatment step, and conversion of the remaining volatile compounds. This strategy is suitable for continuous operation and has been successfully used in processes for obtaining olefins (Gayubo et al., 2010), aromatics (Valle et al., 2010) and hydrogen (Remiro et al., 2013) (Figure 1).
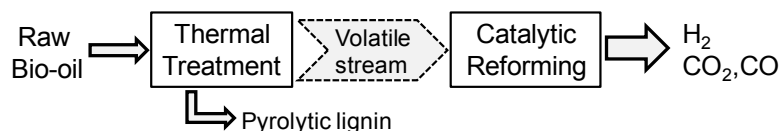

Figure 1: Continuous two-step process for the steam reforming of raw bio-oil.

Therefore, the operation in a continuous two-step reaction system (thermal + catalytic) mitigates the problems related to the SR of raw bio-oil, because it enables the controlled deposition of pyrolytic lignin (in the thermal treatment unit) prior to the fluidized bed catalytic reactor. Given its importance for the overall process, this paper analyses the influence of thermal step operating conditions on the composition of the volatile stream that leaves this unit (i.e., feed to catalytic reactor), and on the amount and composition of the lignin deposited. The effect of thermal step temperature on the Ni-based catalyst behavior (located in the SR reactor) was also studied by analyzing the evolution with time-on-stream of bio-oil conversion and product yields, with the aim of establishing the conditions that lead to a better behavior (higher and more stable H_2 yield).
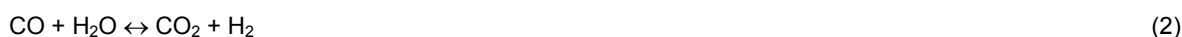
2. Experimental

2.1 Feed and reaction equipment

The effect that thermal step temperature (400-800 °C) and steam-to-carbon ratio S/C (1.5-6.0) have on the composition of exiting volatile stream was analyzed by feeding raw bio-oil ($C_{4.0}H_{6.0}O_{2.9}$), and a mixture of raw bio-oil ($C_{3.5}H_{6.1}O_{3.3}$) with 20 wt% ethanol. The ethanol addition has a stabilizing effect: a low amount (< 5 wt%) prevents aging reactions for a few months of bio-oil storage, while higher amounts (≥ 10 wt%) slows them for at least one year (Diebold and Czernik, 1997). Both raw bio-oils were obtained by flash pyrolysis of pine sawdust in a semi-industrial plant located in *Ikerlan-IK4* technology centre (Alava, Spain), with a biomass feeding capacity of 25 kg/h.

The two-step reaction equipment was previously described (Remiro et al., 2013) and consists of a thermal treatment unit, which is a U-shaped steel tube where the pyrolytic lignin is deposited (in the inlet side), followed by the catalytic fluidized bed reactor, where the thermally treated feed (i.e., the volatile stream leaving the thermal step) is reformed over Ni/La$_2$O$_3$-αAl$_2$O$_3$ catalyst. The raw bio-oil and the bio-oil/ethanol mixture were fed as droplets into the first unit (thermal step) at a feeding rate of 0.1 ml/min (injection pump *Harvard Apparatus 22*) and additional water (that required for setting an S/C ratio) was fed by *307 Gilson* pump. The catalytic SR step was kept at 700 °C, S/C = 6, and space-time (W/F$_0$) = 0.27 g$_{catalyst}$h/g$_{feed}$, which are suitable conditions to achieve high bio-oil conversion and H_2 yield without exorbitant energy cost (Remiro et al., 2013).

2.2 Reaction indices

The SR of bio-oil proceeds according to Eq (1), followed by the water-gas-shift reaction (WGS), Eq (2). The SR of ethanol reaction is expressed by Eq (3). In addition, secondary reactions such as methanation, thermal decomposition, Boudouard reaction and inter-conversion reactions of oxygenates may occur, leading to the formation of by-products (CH_4, CO/CO_2, light hydrocarbons, carbon deposits, other oxygenates).

$$C_nH_mO_k + (n - k) H_2O \rightarrow n\, CO + (n+(m/2) - k) H_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

$$C_2H_6O + 3 H_2O \leftrightarrow 2 CO_2 + 6 H_2 \tag{3}$$

The bio-oil and ethanol conversion is quantified from the molar flow-rate that enters and leaves (un-reacted bio-oil or ethanol) the catalytic reactor, Eq. (4). The H_2 yield is calculated as a percentage of the stoichiometric potential of the feed, Eq. (5). The yield of carbon-containing products (CO, CO_2, CH_4 and C_2-C_4 hydrocarbons) is quantified by Eq. (6).

$$X_i = \frac{F_{i,in} - F_{i,out}}{F_{i,in}} \tag{4}$$

$$Y_{H2} = \frac{H_2 \text{ molar flow}}{\frac{2n+m/2-k}{n} F_{bio-oil,in} + 3 F_{EtOH,in}} \times 100 \qquad (5)$$

$$Y_i = \frac{\text{molar flow of } i \ (CO, CO_2, CH_4, HCs)}{F_{bio-oil,in} + F_{EtOH,in}} \times 100 \qquad (6)$$

3. Results and discussion

3.1 Composition of the thermally treated feed

Table 1 shows the effect of temperature in the thermal treatment unit on the composition of the volatile stream that leaves this step, analyzed by gas chromatography (MicroGC *Agilent 3000*). This stream is composed of gaseous products (Total Gas) and condensable products (Total Liquid). The results of Table 1, which correspond to the feed of bio-oil/ethanol mixture, reveal an almost exponential growth of gaseous compounds as the temperature is raised from 400 to 800 °C, with CO and CO_2 being the major products. These compounds come from the decarbonylation/decarboxylation reactions of oxygenates, which are promoted by increasing temperature. Furthermore, the cracking/decomposition reactions which involve the formation of H_2, CH_4 and light hydrocarbons (mainly ethene) become important above 600 °C.

Regarding the effect of S/C ratio on the composition of the volatile stream when feeding raw bio-oil at 500 ºC (Table 2), it can be observed that an increase of S/C from 1.5 to 3.5 seems to promote the WGS and/or reforming reactions in the thermal step at 500 °C, as suggested by the increase of H_2 and CO_2 content along with a decrease of CO, although practically the same gas yield is obtained for both S/C ratios. However, a further increase in the S/C ratio up to 6.0 leads to a drastic reduction in the formation of CO/CO_2, thereby reducing greatly the total gas yield.

Table 1: Effect of temperature of the thermal step on the composition (wt %) of the product stream. Conditions: Feed, bio-oil/ethanol mixture; S/C, 6.

	400 ºC	500 ºC	600 ºC	700 ºC	800 ºC
H_2	--	--	0.2	0.3	0.5
CH_4	--	0.1	0.4	0.9	1.1
CO	0.3	0.7	2.1	3.6	3.9
CO_2	1.2	1.6	1.8	3.0	4.3
C_2-C_4 Paraffins	--	--	0.1	0.1	0.1
C_2-C_4 Olefins	--	0.1	0.4	0.8	0.7
Total Gas	1.6	2.6	5.1	8.8	10.6
Water	82.6	81.6	81.5	81.3	81.1
Organics	15.8	15.8	13.4	9.9	8.3
Total Liquid	98.4	97.4	94.9	91.2	89.4

Table 2: Effect of S/C ratio of the thermal step on the composition (wt %) of the product stream. Conditions: Feed, raw bio-oil; 500 ºC.

S/C	1.5	3.5	6.0
H_2	0.4	0.8	0.2
CH_4	1.7	1.3	0.4
CO	16.3	12.7	3.7
CO_2	11.9	15.9	4.0
C_2-C_4 Paraffins	0.4	0.3	0.1
C_2-C_4 Olefins	1.6	1.8	0.3
Total Gas	32.2	32.8	8.7
Water	44.1	52.1	78.0
Organics	23.7	15.1	13.3
Total Liquid	67.8	67.2	91.3

Table 3 shows the effect that the thermal step temperature has on the composition (analyzed by GC/MS *QP2010 Shimadzu*) of the liquid fraction collected after volatile stream condensation, when feeding raw bio-oil at S/C = 6. These results evidence the significant effect of raising temperature, especially above 650 °C, with the increase in the phenolic compounds content and the decrease in the levoglucosan content being particularly notable. A remarkable increase in the content of carboxylic acids (mainly acetic) and acetaldehyde is also noticed as the temperature is increased up to 700 °C.

Table 3: Effect of temperature on the concentration of organic compounds (water-free basis) of liquid resulting from the thermal step. Conditions: Feed, raw bio-oil; S/C, 6.

Compounds	Raw bio-oil	500 ºC	550 ºC	600 ºC	650 ºC	700 ºC
Ketones	11.8	10.1	12.8	12.7	20.4	10.8
acetone	*0.4*	*0.3*	*0.5*	*1.0*	*2.3*	*2.6*
1-hydroxy-2-propanone	*6.4*	*4.2*	*6.1*	*6.8*	*13.1*	*6.8*
Acids	25.8	18.5	17.3	23.3	41.1	60.8
acetic acid	*15.3*	*11.3*	*13.5*	*21.1*	*36.1*	*55.8*
Esters	7.3	4.3	5.5	4.4	2.8	1.7
Aldehydes	13.5	4.9	4.9	5.8	9.5	5.2
acetaldehyde	*8.2*	*0.4*	*0.9*	*1.9*	*5.0*	*4.7*
Phenols	5.6	4.8	5.2	5.7	13.0	15.3
Ethers	1.7	0.7	0.4	0.5	1.1	1.0
Alcohols	7.1	3.9	3.6	2.9	2.9	1.6
Sugars	27.2	52.9	50.3	44.8	9.2	3.5
Levoglucosan	*24.3*	*47.7*	*46.0*	*41.8*	*8.3*	*3.2*

3.2 Effect of thermal step conditions on pyrolytic lignin deposition

The effect that thermal step temperature has on the yield and composition (expressed as molecular formula derived from the elemental analysis) of the pyrolytic lignin (PL) deposited is shown in Table 4, for the feed of bio-oil/ethanol mixture at S/C = 6. The effect that S/C ratio has on the PL deposition when feeding raw bio-oil at 500 °C is shown in Table 5. The yield of PL deposited (water-free basis) is calculated by Eq. (7).

$$PL\ Yield(wt\%) = \frac{Pyrolytic\ lignin\ deposited\ (g)}{Bio\text{-}oil\ fed\ (g)} \times 100 \tag{7}$$

Table 4: Effect of temperature on the yield and composition of pyrolytic lignin deposited in the thermal step. Conditions: Feed, bio-oil/ethanol mixture; S/C, 6.

Temperature, ºC	PL yield, wt %	Composition
400	12.6	$C_{6.7}H_{3.8}O_{1.0}$
500	4.5	$C_{7.5}H_{2.8}O_{0.5}$
600	3.5	$C_{7.6}H_{1.9}O_{0.4}$
700	2.0	$C_{7.8}H_{1.0}O_{0.3}$

Table 5: Effect of S/C ratio on the yield and composition of pyrolytic lignin deposited in the thermal step. Conditions: Feed, raw bio-oil; 500 ºC.

Steam-to-carbon ratio (S/C)	PL yield, wt %	Composition
1.5	5.2	$C_{7.1}H_{2.8}O_{0.7}$
3.5	4.4	$C_{7.1}H_{2.8}O_{0.7}$
6.0	4.2	$C_{7.1}H_{2.8}O_{0.7}$

The amount of PL retained and its elemental composition depends to a greater extent on the temperature than on the S/C ratio. Thus, the PL yield decreases markedly from 12.6 wt% to 2 wt% when the temperature is raised from 400 ºC to 700 °C, and its composition tends to be less hydrogenated (Table 4). Nevertheless, the PL deposition is hardly attenuated by increasing the S/C ratio from 1.5 to 6.0 (Table 5), and its elemental composition does not change. A more detailed study on the influence that thermal step temperature has on the composition and properties of the PL deposited was reported elsewhere (Ochoa et al., 2014) in order to establish possible exploitation pathways of this solid material, which would allow a complete valorization of raw bio-oil.

Taking into account that the afore-mentioned results correspond to experiments without catalyst, they must be a consequence of thermal cracking reactions and of possible reactions between oxygenated compounds, which are favored by increasing temperature. It is expected that the change in the volatile stream composition, caused by the thermal treatment temperature and pyrolytic lignin deposition, will influence the results of the subsequent steam reforming step with Ni-based catalyst (Section 3.3).

3.3 Effect of thermal step temperature on the reforming activity of the Ni-based catalyst

Figure 2 shows the effect of the thermal step temperature on the evolution with time-on-stream of bio-oil and ethanol conversion (Graphs a-b), and the yields of H_2 and carbon-containing products (Graphs c-f), obtained in the SR of bio-oil/ethanol mixture in the two-step reaction system (thermal + reforming with Ni/La_2O_3-αAl_2O_3 catalyst). The catalytic step was maintained at 700 °C, S/C = 6, and space-time of 0.27 $g_{catalyst}h/g_{feed}$.
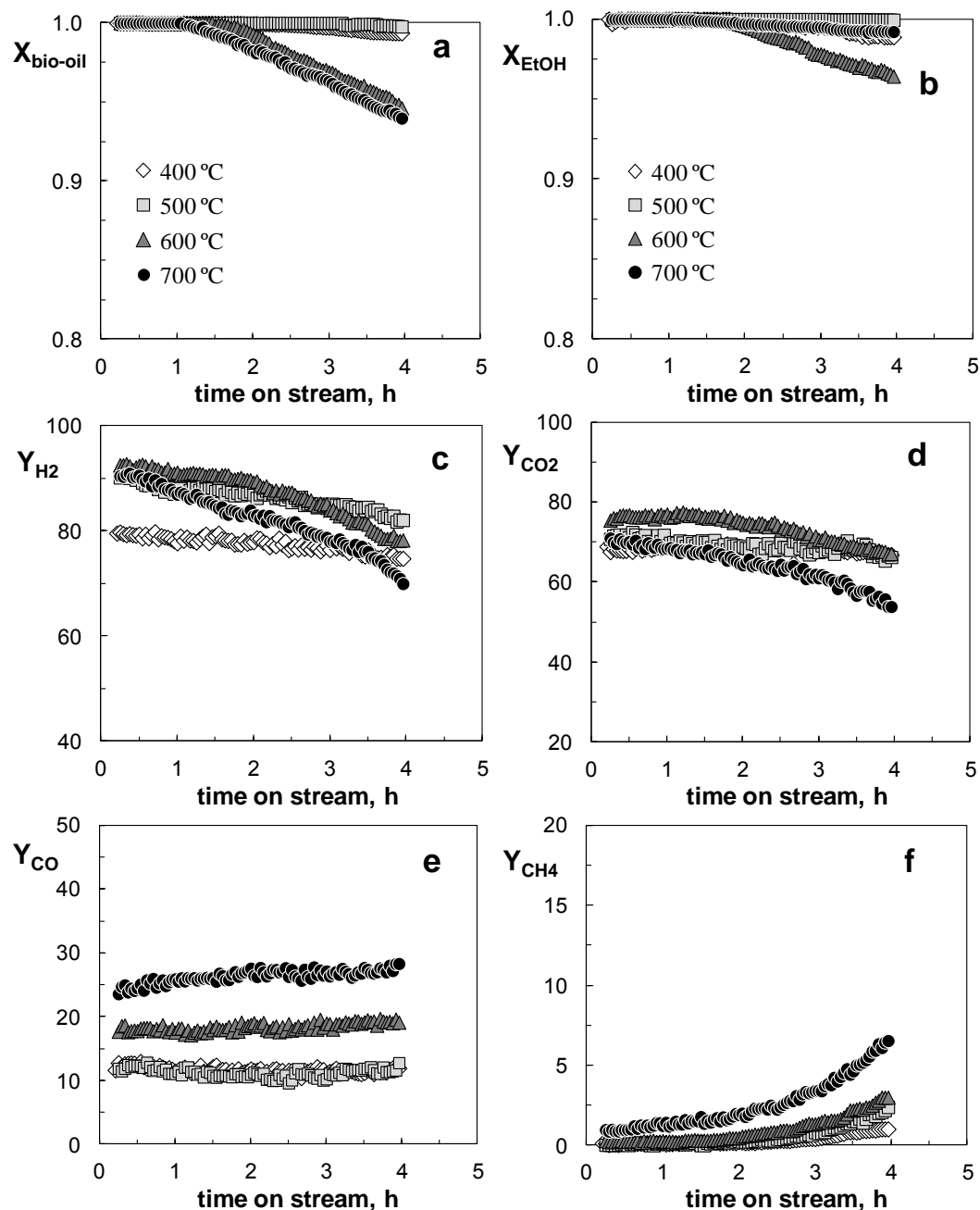

Figure 2: Effect of thermal step temperature on the evolution with time on stream of bio-oil (a) and ethanol (b) conversion, and on the yields of H_2 (c), CO_2 (d), CO (e) and CH_4 (f) during the SR of bio-oil/ethanol mixture. Catalytic step: 700 ºC; S/C, 6; W/F_0, 0.27 $g_{catalyst}h/g_{feed}$.

As shown in Figure 2a, there is a complete initial conversion of the thermally treated bio-oil in the whole range of temperature (400-700 °C), which remains constant for 4 h when the thermal step is carried out at temperatures below 500 °C, and for 1.5 h for higher temperatures. When the thermal treatment is performed at 400 °C, a H_2 yield of around 80 % is obtained (Figure 2c), which remains almost constant in 4 h reaction.

An increase of 100 °C in the thermal unit leads to a remarkable increase of the H_2 yield, thereby obtaining values close to 90 % for temperatures higher than 500 °C, along with low CH_4 yield (Figure 2f) and negligible yields of hydrocarbons (not shown). However, although the thermal treatment at 600 °C involves an initial H_2 yield slightly higher than that obtained at 500 °C, it decreases more sharply with time-on-stream (Figure 2c), with this effect being even more remarkable after thermal step at 700 °C.

These results can be mainly explained by the higher content of phenols, aldehydes and ketones in the stream that enters the catalytic reactor, whose formation in the thermal step is favored by increasing the operating temperature (Table 3), and which causes a rapid deactivation of the catalyst (Aramburu et al., 2014).

4. Conclusions

It has been found that operating temperature in the thermal treatment step (pyrolytic lignin deposition) has a notable effect on the composition of the volatile stream that enters the catalytic reforming reactor, whereas the S/C ratio hardly affects. Thus, increasing the temperature in the range 400-800 °C the gas fraction yield increases (with CO and CO_2 as major compounds, along with H_2, CH_4 and hydrocarbons).

Furthermore, the increase in temperature has consequences on the liquid fraction of volatile stream: i) Above 500 °C, the liquid fraction yield and its total content of oxygenated compounds decrease; ii) its oxygenated composition is different from that of raw bio-oil, with lower concentration of thermally unstable compounds (such as levoglucosan) and higher concentration of phenols (especially above 650 °C), carboxylic acids (mainly acetic acid) and acetaldehyde, which have the negative effect of favoring the reforming catalyst deactivation by coke deposition. In addition, the increase of thermal step temperature decreases the yield of pyrolytic lignin and also its H/C ratio.

Consequently, 500 °C is the thermal step temperature that leads to a better compromise between H_2 yield and Ni/La_2O_3-αAl_2O_3 catalyst stability, with complete and stable bio-oil conversion and H_2 yield close to 90 %.

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