



Note from the field

Strategies for maximizing the bio-oil valorization by catalytic transformation



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ABSTRACT

A study was carried out on the continuous thermal treatment of raw bio-oil and of its aqueous fraction (obtained by adding water) based on the interest of this strategy for separating the pyrolytic lignin, which enhances the valorization of the treated bio-oil in a subsequent *in-line* catalytic step. It was determined that after the direct thermal treatment of raw bio-oil, 77 wt% oxygenates originally contained in the bio-oil are capable of catalytic valorization, whereas after the treatment of the bio-oil aqueous fraction, 64 wt% of bio-oil oxygenates are amenable to further valorization.

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1. Introduction

The biomass-based resources will play a key role in mitigating the strong dependence on fossil carbon in the chemical and petrochemical industries. 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 (Liu et al., 2012).

The liquid product (bio-oil) obtained by fast pyrolysis of biomass has an essential role as raw material within the bio-refinery scheme, together with other fuels or intermediate raw materials (H₂, bio-ethanol, bio-gas, synthesis gas, etc.) also derived from biomass.

Nevertheless, the feasibility of bio-oil catalytic transformation (e.g., by catalytic cracking, co-feeding in FCC and steam reforming) is curtailed by the problems associated with re-polymerization of some compounds during bio-oil vaporization (Gayubo et al., 2005), which causes the deposition of a solid (pyrolytic lignin, PL). This deposition creates blocking problems in the operation system (inlet tubes and reactor) and it also affects the catalyst deactivation. Several solutions have been proposed in the literature aimed at solving these problems: i) Methanol co-feeding, which is

interesting due to the stabilizing effect of alcohols addition during the bio-oil storage (Czernik et al., 2007), and due to the synergies between the bio-oil and methanol transformation (Gayubo et al., 2009); ii) Bio-oil pre-treatment by water addition at several weight ratios, such as 2:1 (Czernik et al., 2002; Basagiannis and Verykios, 2007) and 1.5:1 (Kechagiopoulos et al., 2009), which separates the bio-oil into an aqueous fraction (predominantly carbohydrate-derived) and an organic (lignin-derived) fraction (Garcia et al., 2000). The aqueous fraction contains lighter compounds, so that less PL deposition is expected during its volatilization, compared to the raw bio-oil volatilization (Gayubo et al., 2004); iii) Bio-oil pre-treatment by accelerated aging at temperatures below 100 °C (Oasmaa et al., 2004); iv) Utilization of a process with two steps in series (thermal treatment + catalytic transformation) (Gayubo et al., 2010).

The two-step strategy (thermal treatment + catalytic transformation) allows the separate and controlled deposition of pyrolytic lignin in the first reactor (thermal treatment), during the volatilization of both bio-oil aqueous fraction (Remiro et al., 2013a) and raw bio-oil (Remiro et al., 2013b).

The PL that is obtained in the thermal step is interesting as a raw material. Apart from heat and power generation, a wide range of strategies for valorizing different type of lignins (e.g., alcell, kraft and organosolv) have been reported in the literature aimed at obtaining bio-fuels and chemicals. There are some studies on the use of kraft-type lignins as catalyst support, after activation with H₃PO₄, in processes such as toluene oxidation (Bedia et al., 2010)

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and olefins hydrogenation over Pd-based catalysts (Guillén et al., 2009). Qin and Kadla (2012) studied the use of “activated” kraft lignin as precursor in the production of carbon fibers. An extensive review of different strategies for the production of chemicals by catalytic conversion of lignin was published by Zakzeski et al. (2010).

In this paper, the continuous thermal treatment of a bio-oil stream was studied by analyzing the effect of temperature on the amount and nature of PL deposited (by thermogravimetry and elemental analysis), and on the composition of the stream exiting the thermal unit. The main objective of this paper is to determine the most suitable strategy for maximizing the yield of oxygenates, originally contained in the raw bio-oil that are amenable to valorization in a subsequent catalytic step.

2. Experimental

The raw bio-oil was obtained by flash pyrolysis of pine sawdust in a semi-industrial demonstration plant (Fernández-Akarregi et al., 2013). The aqueous fraction was obtained by phase separation after adding water to this raw bio-oil, in water/bio-oil mass ratio = 2/1 (Czernik et al., 2002). The raw bio-oil is separated into two fractions: *aqueous fraction* and *organic fraction* (which contains 23 wt% of the raw bio-oil oxygenates).

The composition of the raw bio-oil and of the aqueous fraction was previously determined by GC/MS analysis (Remiro et al., 2013a). The composition of the thermally treated bio-oil was also analyzed by this method.

The thermal treatment was performed in a U-shaped tube (S-316 stainless steel, 5/8" internal diameter) in the 200–600 °C range (thermal step in Fig. 1). The bio-oil (raw bio-oil or bio-oil aqueous fraction) was fed continuously in the form of droplets that are entrained by the carrier flow (He).

The analysis of the volatile stream that leaves the unit was performed continuously by gas micro-chromatography (Agilent μ GC 3000).

The chemical composition (C, H, O) of the PL samples obtained at different temperatures was determined by elemental analysis (Leco CHN-932 analyzer and ultra-microbalance Sartorius M2P).

3. Results and discussion

3.1. Pyrolytic lignin yield and composition

The effect of temperature on the yield of PL deposited in the thermal treatment unit (wt%, referred to the oxygenates fed in the

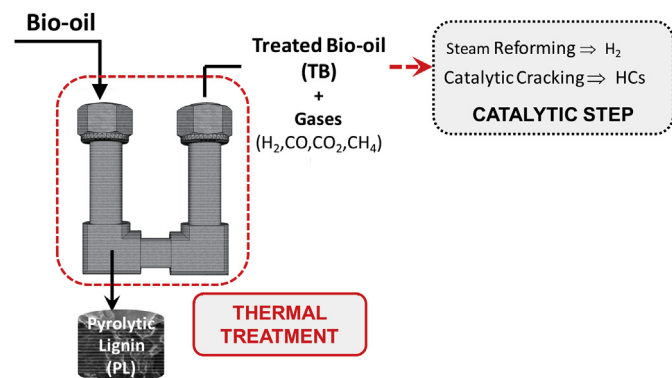


Fig. 1. Scheme of the two-step system for the bio-oil thermal treatment followed by in-line catalytic transformation of the treated bio-oil.

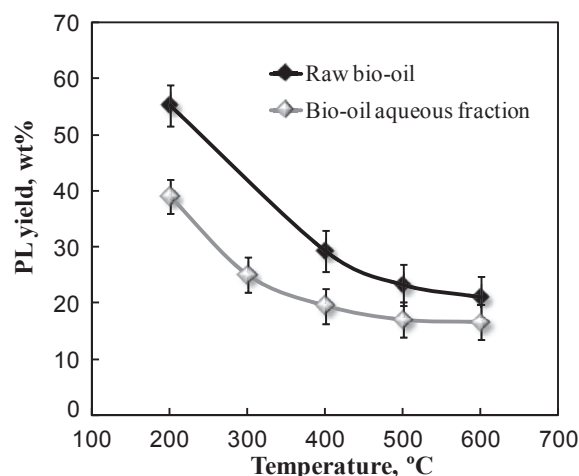


Fig. 2. Effect of operating temperature on the yield of pyrolytic lignin deposited by feeding raw bio-oil and bio-oil aqueous fraction.

bio-oil) is shown in Fig. 2 for both the raw bio-oil and the bio-oil aqueous fraction. The PL yield was quantified by Eq (1).

$$\text{PL yield (wt\%)} = \frac{\text{lignin deposited (g)}}{\text{bio-oil fed (g)}} \times 100 \quad (1)$$

The PL yield decreases considerably in the 200–400 °C range for both the raw bio-oil (from 55 wt% to 30 wt%) and the aqueous fraction (from 38 wt% to 20 wt%), with this effect being less significant above 400 °C. It can be observed that PL yields are significantly lower when the bio-oil aqueous fraction is fed, but this difference is lower as the temperature is increased (only 6 wt% for the PL deposited at 500 °C). This result can be explained by the increase in temperature, which attenuates the involvement of heavy oxygenates in the PL formation.

Most of the bio-oil compounds with low–medium molecular weight volatilize in the 100–200 °C range. The re-polymerization of certain bio-oil oxygenates (mainly those derived from the lignin contained in biomass) also occurs between 100 °C and 200 °C. When the bio-oil heating temperature reaches around 110 °C the PL formation begins, firstly as a viscous carbonaceous product due to the significant presence of liquid oxygenates.

Fig. 3 shows the elemental analysis results of the PL samples deposited during the thermal treatment at different temperatures by feeding the bio-oil aqueous fraction (Fig. 3a) and raw bio-oil (Fig. 3b). It can be noted that C, H and O contents in the PL deposited at 200 °C from both feeds are similar, and they are also very similar to the elemental composition of the raw bio-oil (i.e., 51.6 wt% C, 7.2 wt% H, 41.6 wt% O). This fact also suggests that the PL obtained at 200 °C consists of non-volatilized bio-oil compounds that are retained during its formation.

There is also a progressive increase in the C content and decrease in H and O contents with temperature. This trend is observed in the PL samples obtained from both the bio-oil aqueous fraction (Fig. 3a) and the raw bio-oil (Fig. 3b), although the PL samples coming from the raw bio-oil have slightly higher C contents. The PL deposited at 600 °C has a more graphitic nature (with significantly lower H and O contents), which suggests that thermal cracking reactions occur during its deposition, with the consequent formation of CO/CO₂ and CH₄.

The CHO elemental composition of PL and gaseous products formed in the thermal treatment affects the composition of the

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