Treatment and Valorization to hydrogen of the aqueous fraction of bio-oil from lignocellulosic biomass pyrolysis by aqueous phase reforming

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Objectives and novelty

The aqueous fractions of pyrolysis bio-oils (AFBs) have a high water content (75-90 wt%) and include a wide variety of polar organic compounds, which makes difficult their valorization or management as a waste stream by conventional processes. Promising technologies, such as aqueous phase reforming (APR), are currently being developed to valorize this type of streams. APR is a catalytic process in aqueous solution whereby an organic substrate reacts with water to produce a gas phase (mainly composed by H_2 and CO_2) and a liquid effluent. The process provides several advantages over steam reforming (SR): a significant reduction in energy consumption (as it is carried out under milder operating conditions and in liquid phase, therefore avoiding the vaporization of the feed stream), easier separation of the H_2 generated (since no significant amount of CO is usually present in gas product due to the water-gas shift reaction is highly favoured at process operating conditions), etc. However, most of the studies published in the literature were performed using model compounds (or mixtures of them) as process feedstock.

The main objective of this Doctoral Thesis was the treatment and valorization to H_2 of the AFB from lignocellulosic biomass pyrolysis by APR process. Initially, a representative composition of AFBs was established, based on the relevant literature in the field. Then, the APR of each individual compound and mixtures of them was studied, selecting the optimal operating conditions. In addition, the stability of the catalyst was evaluated, as well as the possible relationship between the structure of the catalyst metal phase and the H_2 production. On the other hand, a technical-economic study of the APR of AFB was carried out, evaluating different approaches to the process according to the gas valorization possibilities. Finally, the APR of real AFBs was studied and the H_2 production obtained was related to the catalytic pyrolysis operating conditions.

Results

The first section of this Thesis was reported as the paper entitled “Aqueous-phase reforming of water-soluble compounds from pyrolysis bio-oils” [1], and it was focused on the APR of levoglucosan, hydroxyacetone, furfural and acetic acid (compounds usually present in AFBs), under different operating conditions. The experiments were carried out in batch mode and using Pt impregnated at 3 wt% on ENSACO250 carbon black (CB) as catalyst. Different initial organic matter concentrations (1-5 wt%), temperatures (175-220 ºC) and reaction times (0.5-4 h) were studied. The best results were obtained at 1 wt%, 220 ºC and 4 h. The highest carbon-to-gas conversion (CCgas) and H_2 production and selectivity values were obtained for hydroxyacetone, which was mainly converted to H_2, CO_2 and CH_4. However, levoglucosan was mostly transformed to H_2 and CO_2, while furfural and acetic acid mainly yielded CO_2 and different alkanes. These results were explained through different proposed reaction mechanisms. The catalyst exhibited high stability during five successive 4 h reaction cycles, using levoglucosan as feedstock, with only a slight decrease in Total Organic Carbon (TOC) conversion.

In the second section, presented as “Valorization to hydrogen of bio-oil aqueous fractions from lignocellulosic biomass pyrolysis by aqueous phase reforming over Pt/C catalyst” [2], the APR of several binary and multicomponent mixtures, as models of different AFB compositions, was studied. A strong dependence between the feedstock composition and H_2 production was observed, as the presence of furfural and acetic acid hindered APR, while the highest H_2 yields were obtained with levoglucosan- and hydroxyacetone-rich AFBs. In addition, the presence of minority compounds such as formic acid enhanced the reforming of the whole AFB, increasing H_2 production by more than 50 %. On the other hand, the catalyst activity remained almost constant over 5 consecutive reaction cycles. TPD characterization of the used catalysts showed an increasing mass loss with reaction cycles, related to the cumulative adsorption or deposition of reaction products. In addition, the Pt nanoparticles underwent morphological changes during reaction cycles, increasing the prevalence of low-coordination active sites (located at structural defects, step-edges, etc.), yielding higher H_2 production during cycles 2 and 3. It was found that, the presence of the H_2 generated in the first cycles, the acidic medium and the APR operating conditions led to these morphological changes.

The third chapter, “Energy and economic analysis of alternatives for the valorization of hydrogen rich stream produced in the aqueous phase reforming of pyrolysis bio-oil aqueous fraction” [3], was aimed at evaluating the potential feasibility of the APR technology. The process modelling was performed

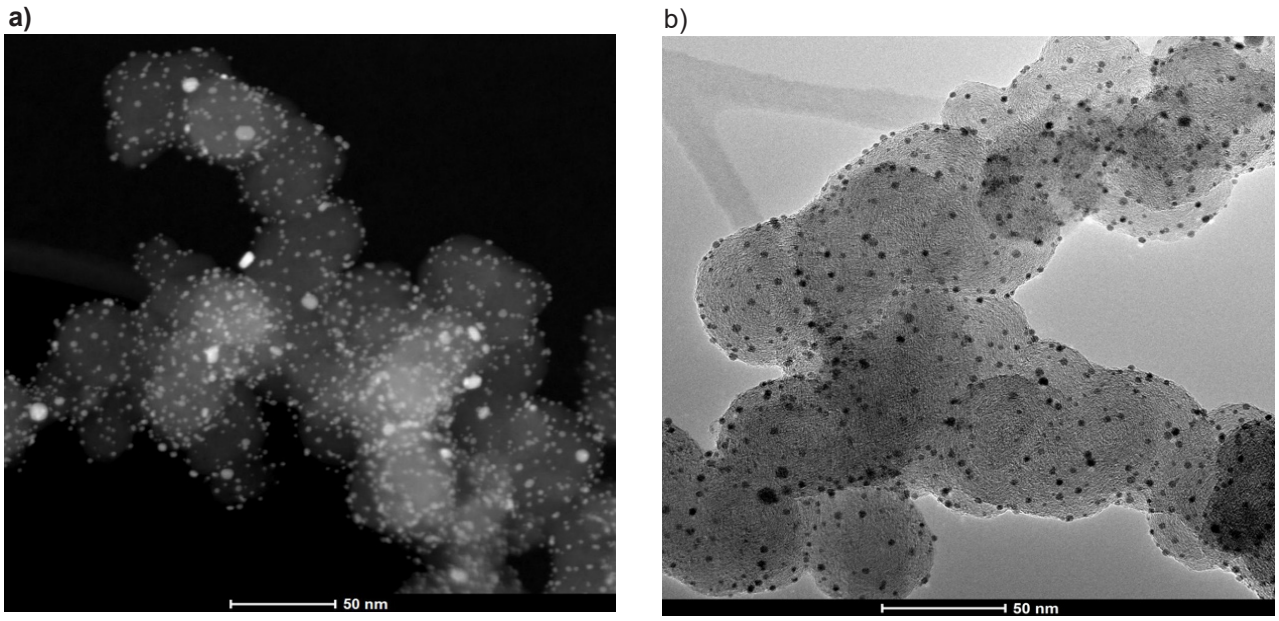

Figure 1. STEM/TEM images of fresh Pt/CB catalysts with a metal load of: a) 3 and b) 5 wt%.

using computational simulation tools (Aspen HYSYS), based on the experimental results reported in the previous paper for the most complex AFB composition. For this purpose, a specific thermodynamic model was developed to properly estimate the properties and phase equilibria of the AFB. Different process alternatives for the valorization of the APR gas stream, based on its commercialization, energy recovery or a combination of both, were technically and economically evaluated, detecting a significant energy cost reduction by means of an adequate heat integration. The economic optimum was achieved using a small fraction of the APR gas for energy self-covering and commercializing the rest as crude H_2. For this case, a production cost of ca. 1.5 €/kgH_2 was estimated, suggesting the H_2 produced by APR as potentially competitive with green H_2.

The fourth and last section of the Thesis, was published as "Understanding the relationship between catalytic pyrolysis conditions and hydrogen production by aqueous phase reforming of the water-soluble fractions of bio-oils" [4] and carried out in collaboration with the Thermochemical Processes Unit at IMDEA Energy Institute (Móstoles, Madrid). The main objective of the work was to study the APR of three real AFBs obtained by catalytic fast pyrolysis of oak woodchips at different conditions, using Pt contents in the catalyst of 3 and 5 wt% (Figure 1).

The best results were obtained for the AFB with the highest levoglucosan and the lowest acetic acid concentration, reaching up to 46 mol% H2 in the APR gas. It was proved that the H2 yield by APR was related to the AFBs composition and, in turn, to the catalytic pyrolysis conditions: more severe pyrolysis conditions provided with AFBs more favourable to the APR and, consequently, with a higher H2 production and a treated effluent with a lower organic load. Moreover, as previously observed for synthetic AFBs, the addition of formic acid (0.04 %wt) led to a synergistic effect on the AFB reforming, increasing H2 production by 40 %. Finally, the stability of the 5 wt% Pt catalyst was evaluated over 3 consecutive reaction cycles. A small decrease in TOC conversion and CCgas was observed, although a more significant reduction in H2 production. TPD analyses of the used catalysts showed an increasing mass loss with reaction cycles and TEM characterization, a small increase in the mean nanoparticle size after cycle 3.

Conclusions

The initially selected AFB representative compounds showed very different behaviour as individual APR substrates: hydroxyacetone provided the highest H_2 production, whereas furfural and acetic acid were transformed mainly to C_3H_8 and CH_4, respectively. The Pt/CB catalyst showed a high stability in the levoglucosan APR after 20 h of use. Moreover, the reforming of synthetic binary mixtures suggested a possible selective adsorption of one of the compounds, preventing the reforming of the mixture. Minority compounds, such as formic acid, showed a synergistic effect on the APR of the mixtures, increasing TOC conversion, CCgas and H_2 production. Likewise, the presence of the H_2 generated over the cycles, the acidic medium and the operating conditions induced a higher prevalence of low-coordination centres in the metal nanoparticles of the catalyst and an increase in H_2 production. On the other hand, the energy and economic analysis of the process showed that the use of AFB as feedstock combined with an adequate integration and heat recovery results in a potentially feasible technology to produce bio-H_2, at a competitive cost (1-2 €/kg). Finally, the APR of real AFBs improved with high concentrations of levoglucosan and was hampered by the presence of acids and ketones. The relationship between severe operating conditions of catalytic pyrolysis and a higher H_2 valorization of the AFB was established.

Related publications

[1] Justicia J, Baeza JA, Oliveira AS, Calvo L, Heras F, Gilarranz MA, Aqueous-phase reforming of water-soluble compounds from pyrolysis bio-oils, Renewable Energy, 2022; 199, 895-907. *https://doi.org/10.1016/j.renene.2022.09.021*

[2] Justicia J, Baeza JA, Calvo L, Heras F, Gilarranz MA, Valorization to hydrogen of bio-oil aqueous fractions from lignocellulosic biomass pyrolysis by aqueous phase reforming over Pt/C catalyst, Chem Eng J, 2023; 477, 146860. *https://doi.org/10.1016/j.cej.2023.146860*

[3] Heras F, Justicia J, Baeza JA, Gilarranz MA, Ferro VR, Energy and economic analysis of alternatives for the valorization of hydrogen rich stream produced in the aqueous phase reforming of pyrolysis bio-oil aqueous fraction, Bioresour Technol, 2024; 399, 130572. *https://doi.org/10.1016/j.biortech.2024.130572*

[4] Justicia J, Heras F, Moreno I, Baeza JA, Calvo L, Fermoso J, Gilarranz MA, Understanding the relationship between catalytic pyrolysis conditions and hydrogen production by aqueous phase reforming of the water-soluble fractions of bio-oils, Energy Convers Manage, 2024; 320, 118999. *https://doi.org/10.1016/j.enconman.2024.118999*

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