

From waste to value: aqueous phase reforming of lignin-HTL by-products

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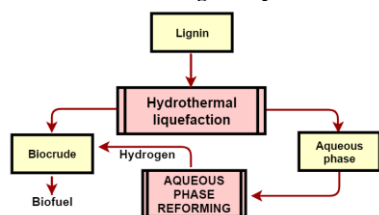
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Introduction

Hydrothermal liquefaction (HTL) of biomass is a strategic process to convert renewable feedstocks into a biofuel (i.e. biocrude) [1]. Despite their importance, the research has not deeply investigated the aqueous side-streams, that may contain up to 30% of the carbon present in the feed [2]. The highly diluted current coming out from HTL is hardly exploitable through selective recovery, or by distillation. For this reason, aqueous phase reforming (APR) may be a key process to convert the organics into a gas phase rich in hydrogen [3]. In turn, it may be used to perform the upgrade of the biocrude, reducing its oxygen content by hydrodeoxygenation, theoretically avoiding the hydrogen requirement of the plant from external facilities (Figure 1).

Figure 1. Block flow diagram of an HTL-APR integrated plant



In the present work, representative compounds and actual liquid phase coming from the HTL of lignin have been tested at different reaction temperatures (230-270 °C) with a commercial 5% Pt/Al₂O₃ catalyst. The intrinsic tendency toward hydrogen production of several molecules belonging to different class of compounds (carboxylic and bicarboxylic acids, alcohols, hydroxyacids, ketones, aromatics) has been investigated. Together with the gas phase, a thorough characterization of the liquid phase was performed to determine key intermediates/by-products present at the end of the reaction.

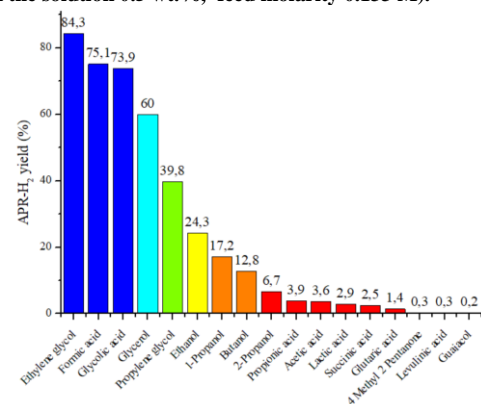
Materials and Methods

The catalytic tests have been performed in a Parr bench top reactor, equipped with a temperature controller. The screening of seventeen compounds was performed at equimolar concentrations. At the end of the reaction, the gas phase was collected in a sampling syringe and the analysis performed by an SRA μ GC. The liquid phase was characterized by HPLC Shimadzu system, equipped with a Rezex ROA organic acid column. The quantification of the compounds was performed *via* external calibration.

Results and Discussion

In Figure 2 the hydrogen yield (defined as the ratio between the moles of hydrogen present in the gas phase and the moles theoretically obtained according to the reaction stoichiometry) at 270 °C of the seventeen representative compounds is reported. Two main outcomes are worthy of consideration. First of all, carboxylic acids showed low conversion and tendency to hydrogen production, leading to a gas phase rich in alkanes. On the other hand, glycolic acid, one of the most present compounds in the aqueous phase post hydrothermal processing ([2]) showed the third highest H₂ yield. To the best of our knowledge, glycolic acid has never been subjected to APR before of this work.

Figure 2. APR hydrogen yield (reaction conditions: temperature 270°C, reaction time 2 h, catalyst loading in the solution 0.5 wt.%, feed molarity 0.133 M).



Significance

It is estimated that in the hydrothermal processes the cost of the waste water disposal is second only to the feedstock costs [4]. Moreover, the main source of the hydrogen used in a biorefinery still comes from fossil nature, in big centralized plants. Valorizing the aqueous by-products aiming to produce the required hydrogen of a biorefinery (i.e. for deoxygenation reactions) would solve two critical issues connected with their development.

Acknowledgments

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