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# Aqueous phase reforming of biorefinery side-streams: challenges towards the industrial application

## Abstract

The challenge for sustainable and renewable sources of energy passes through the use of biomass. The biorefineries aim to convert the conventional technologies of the fossil-based industry to the more complex exploitation of biomass. One of the key bottlenecks is the complete valorization of their organic content, often lost in the aqueous side streams. Aim of the present work was the investigation of the aqueous phase reforming process in order to convert carbon-laden water fractions into a gas mixture rich in hydrogen, looking at three different kind of starting materials.

Alginate was tested as representative of the sugar fraction derived from aquatic biomass. The influence of several operating conditions was investigated (catalyst and alginate loading, reaction time, reaction temperature, hydrogen partial pressure, pH) towards the hydrogen selectivity, hydrogen yield and carbon conversion to gas. Among the results, it was observed that more diluted solutions allowed the carbon conversion to be increased, while a maximum was observed for the hydrogen selectivity. The production of hydrogen reached a plateau, due to the formation of intermediate liquid products recalcitrant for hydrogen formation. Finally, the higher pH led to higher hydrogen yield, reducing the dehydration pathways responsible for the decrease of selectivity.

Seventeen compounds belonging to different classes of molecules (carboxylic and bicarboxylic acids, hydroxyacids, aromatics, alcohols and polyalcohols, ketones) have been selected to be representative of the carbon-laden aqueous streams derived from hydrothermal liquefaction of lignocellulosic biomass. The study focused initially on the influence of the reaction temperature on the performance. The investigation consented to define a scale of reactivity among the seventeen compounds. Glycolic acid, one of the most present compounds in the HTL-derived wastewater, reported one of the highest hydrogen yields, with the gas phase composed only by hydrogen and carbon dioxide. On the other hand, acetic acid, representative of carboxylic acids, catalytically decomposed into carbon dioxide and methane, with a negligible production of hydrogen. Binary and ternary synthetic mixtures have been tested, highlighting competitive adsorption issues. Tests performed at different reaction time suggested possible reaction pathways for glycolic acid, acetic acid and lactic acid. Moreover, the study of the ternary mixture pointed out the differences in reactivity because of the adsorption, while the selectivity remained analogous to the single-compound tests. The aqueous phase derived from the hydrothermal liquefaction of a lignin-rich stream was subjected to APR. It was found that the reaction performance was linked with the aromatic content. For this reason, diethyl-ether was used to perform a liquid-liquid extraction, reducing the presence of aromatics and improving the hydrogen yield.

Finally, the sugar-laden aqueous phase derived from an industrial bioethanol plant was investigated, suggesting an alternative pathway of valorization for the hemicellulose fraction of lignocellulosic biomass. The influence of temperature and carbon concentration was studied initially on the model compounds (glucose, xylose, sorbitol and xylitol) and afterwards on the industrial hydrolysate, showing that the hydrogen yield increased with the reaction temperature and at more

diluted concentrations. In this case, no adsorption issues were observed, being the experimental results obtained in the case of binary mixtures analogous to the ones from the linear combination of single-compounds tests. Given that the sugar alcohols are more prone to hydrogen production, a pretreatment of the sugar solution was performed to convert them selectively to the corresponding alcohols. A net hydrogen production was obtained at different carbon concentration.

The research performed allowed to look at the aqueous phase reforming as a possible process for the valorization of aqueous by-products in the biorefinery context. The main findings showed that it may be possible to reduce the waste production converting the organic content of by-products into a valuable gas, decreasing the external need of hydrogen of a biorefinery.