

Towards the sustainable hydrogen production by catalytic conversion of C-laden biorefinery aqueous streams

Giuseppe Pipitone¹, Giulia Zoppi¹, Simone Ansaloni¹, Samir Bensaid¹, Raffaele Pirone^{1*}

¹ Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli

Abruzzi 24, 10129, Turin, Italy.

*Corresponding author: raffaele.pirone@polito.it

Highlights

- An extensive screening of characteristic compounds was performed.
- The alcohols were the most performant species towards hydrogen production.
- A two steps hydrogenation-APR scheme was investigated.
- A real biorefinery stream was subjected to APR.

1. Introduction

The hydrothermal treatment of biomass has been explored with the aim of producing alternative fuels [1]. The focus of the research is maximizing the quantity and quality of the oil phase. However, it is recognized that, to fulfill the economic sustainability of the entire process, the aqueous phase must be valorized thanks

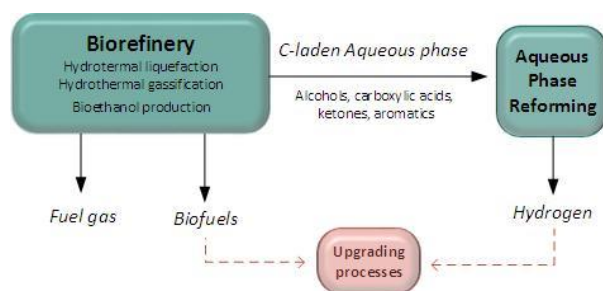


Figure 1. Scheme of the sustainable production of hydrogen from biorefinery streams and its possible use.

to its organic content. The literature often does not have many information about its characterization [2]. The complexity of the mixture requires the development of a process able to convert, as a whole, the organic matter. In this sense, aqueous phase reforming (APR) is a promising process able to convert oxygenated hydrocarbons in a gas mixture rich in hydrogen. It can be used for a number of applications, including biofuels upgrading (Figure 1). For these reasons, we began an extensive investigation of characteristic compounds that can be found in the C-laden aqueous phase generated in a hydrothermal process. Moreover, mixtures of these species were tested to verify the influence of possible reactions between the different classes on the hydrogen yield. A catalytic step before the reforming was investigated to increase the global hydrogen yield (not detailed here). Finally, real aqueous biorefinery streams were subjected to APR. To the best of our knowledge, no other previous work has evaluated so many species (around 20, namely carboxylic acids, ketones, alcohols, aromatics, aldehydes, sugars, sugar alcohols) in one experimental apparatus. Therefore, this work aims to gain knowledge for the design of an efficient catalyst able to valorize the aqueous sub-products of a hydrothermal process.

2. Methods

The experimental apparatus used for the APR tests and the analytical methods used to characterize the liquid and gas products are described elsewhere [3]. The selected results included in this abstract were performed in a Parr batch reactor at: 230, 250, 270°C; 2 hours reaction time; 1%_{wt} organic content in the liquid feed; 0.5%_{wt} catalyst in the liquid (5%Pt on Al₂O₃). The hydrogen selectivity is the ratio between the moles of H₂ and total hydrogen in the gas phase (hydrogen in H₂ and in alkanes); the carbon to gas conversion is the ratio between the carbon measured in the gas phase via GC analysis and the initial carbon in the organic feed.

3. Results and discussion

In Figure 2 some of the results obtained are showed. In 2.A the Carbon to Gas and the H₂ selectivity at the different investigated temperatures are reported for some peculiar compounds: it emerges how carboxylic

acids, ketones and aromatics are recalcitrant to APR in terms of H₂ selectivity, contrary to alcohol group-containing molecules. In 2.B the same parameters are presented for a three-compounds mixture (the ideal point considers the linear combination of the individual molecule performances), where it can be seen that the addition of low activity molecules (i.e. acetic acid) worsens the conversion activity also of the most reactive ones (namely, glycolic acid), but not the H₂ selectivity. In 2.C the TGA of some spent catalysts under air flow shows that high temperature oxidation of organic matter (presumably coke-like residues) occurs, which is around 5-8%_{wt} of the original organic content in the feed (from C-balance closure via liquid TOC and gas GC analysis). Moreover, the liquid phase recovered from the reaction is characterized by HPLC (see in 2.D. glycolic acid and acetic acid, the latter being also a liquid product of glycolic acid APR).

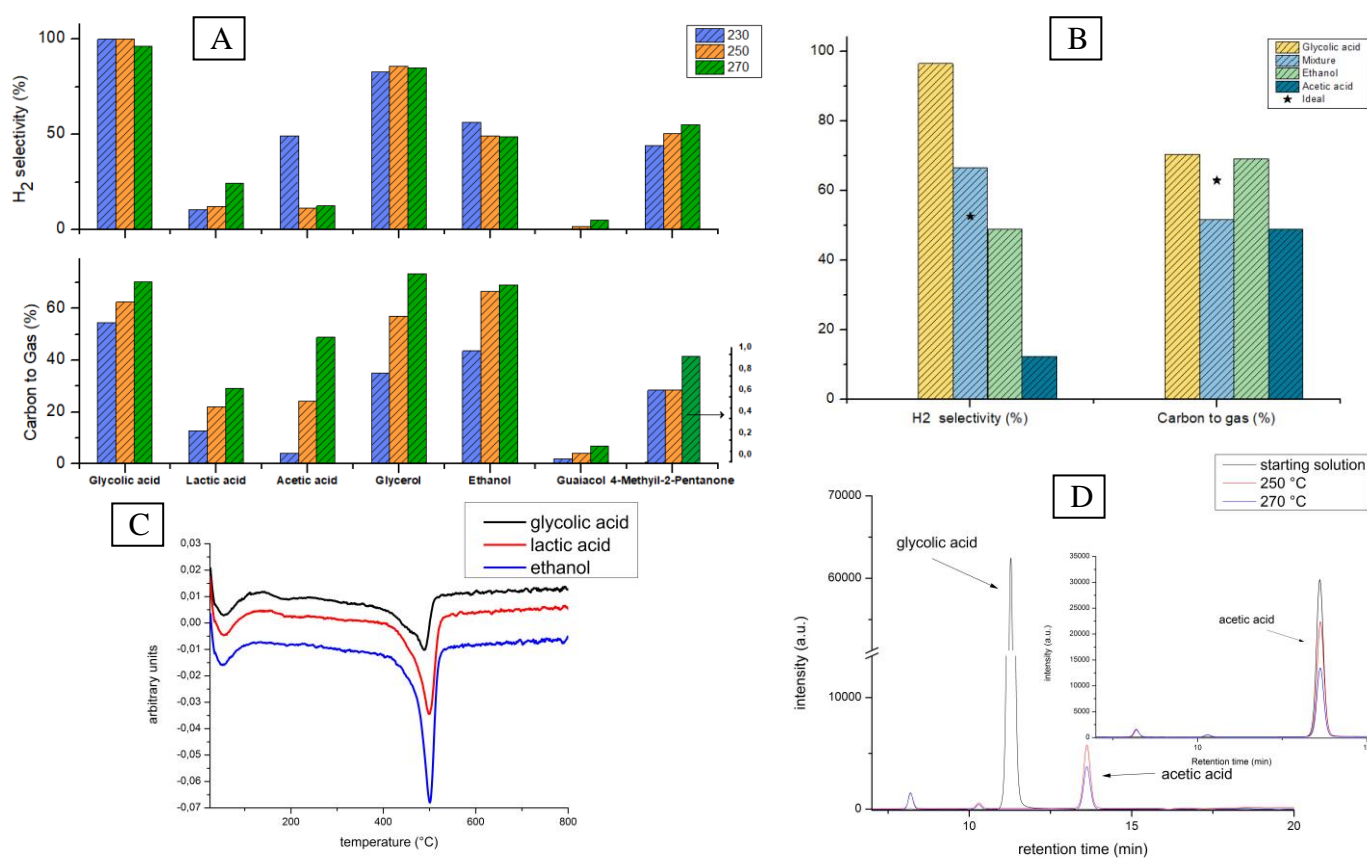


Figure 2. Some selected results from APR of representative compounds (see Methods for details).

4. Conclusions

The APR of compounds present in the aqueous stream of a biomass hydrothermal process was performed. In order to approach the industrial application, a real and complex biorefinery aqueous stream was tested and its performance evaluated. The study allowed to recognize classes of compounds that, as such, cannot be valorized for the production of hydrogen, which suggests to find complementary catalytic functionalities to “activate” the APR-recalcitrant compounds. The gathered information can help to have a deeper understanding in the process to valorize effectively the aqueous phase produced in a hydrothermal process.

References

- [1] S.S. Toor, L. Rosendahl, A. Rudolf, Energy 36 (2011) 2328–2342.
- [2] E. Panisko, T. Wietsma, T. Lemmon, K. Albrecht, D. Howe, Biomass and Bioenergy 74 (2015) 162–171.
- [3] G. Pipitone, D. Tosches, S. Bensaid, A. Galia, R. Pirone, Catal. Today (2017).

Keywords

Aqueous phase reforming; Hydrogen production; Hydrothermal process; Biorefinery.