

Renewable H₂ production by aqueous phase reforming of ethanol-rich wastewaters

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11th international conference on sustainable solid waste management - Abstract

Introduction

Biorefinery processes have gained significant importance as alternative approaches to replace fossil fuels and efficiently manage waste streams, contributing to sustainable and economically viable energy production and waste valorization [1]. Consistent with this role, aqueous phase reforming (APR) process aimed to explore H₂ production from renewable resources. APR is a liquid thermo-catalytic process for the conversion of oxygenated compounds into H₂ and CO₂ in the presence of an heterogenous catalyst. Small alcohols and polyols have demonstrated been promising starting materials in terms of H₂ productivity [2]. A compelling strategy involves the utilization of second-generation feedstocks, like bio-ethanol, which is frequently present in wastewaters from lignocellulosic and food waste fermentations processes [3]. In this scenario, APR generates a H₂ rich gas phase while purifying industrial wastewaters for further use or disposal, maintaining a CO₂-neutral process, by utilizing the CO₂ released during APR for biomass growth. Presently, biological processes, such as anaerobic digestion, represent the default wastewater treatment technologies to convert organic residues into biofuels, mainly bio-CH₄ and bio-H₂. However, APR presents a valuable alternative that eliminates the need for significant storage capacity, a requirement in anaerobic digestion processes. However, H₂ selectivity represents the major challenge in the APR process. The catalyst used, the method of synthesis and the operative conditions all play a significant role in this process. Metal catalysts reported high H₂ selectivity, particularly Pt-based catalysts for their low methanation activity and Ru-based catalysts for their C-C bond breaking activity. APR catalysts must exhibit C-C over C-O bond breaking capacity, which favor water gas shift reactions (WGS) aimed at reducing CO content and boost H₂ production [4]. Consequently, batch experiments were carried out to elucidate the catalytic activity of Ru and Pt-based catalyst in the APR reaction of ethanol. Alternative synthesis methods will be tested (e.g., exsolution) and the optimal operative conditions will be addressed with the objective to develop a cheap, active and stable catalyst, suitable for ethanol rich wastewaters valorization and commercialization.

Material and methods

The APR tests were conducted in a 300 mL 4560 batch reactor with 1 - 3 wt. % of ethanol and an inert atmosphere between 200 – 270 °C and an autogenous pressure (15 – 55 bar). Four commercial catalysts were investigated (Pt/C, Ru/C, Pt/Al₂O₃ and Ru/Al₂O₃) for the catalytic activity tests. HPLC (Shimadzu) and micro-GC (SRA) analysis were carried out for liquid and gas samples, respectively. Moreover, catalyst characterization pre and post-APR was studied with XRD, XPS, BET and TPR/TPD techniques. APR performance was evaluated through ethanol conversion (Eq.1), H₂ productivity (Eq.2), H₂ selectivity (Eq.3) and carbon to gas (Eq.4).

$$\text{Conversion (\%)} = 100 * \frac{|EtOH_i| - |EtOH_f|}{|EtOH_i|} \quad \text{Eq.1}$$

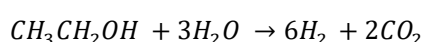
$$\text{H}_2 \text{ productivity} \left(\frac{\text{mmol}}{\text{mol}} \right) = \frac{\text{mmol}_{\text{final}} \text{H}_2}{\text{mol}_{\text{in}} \text{C}_{\text{feedstock}}} \quad \text{Eq.2}$$

$$\text{APR H}_2 \text{ selectivity (\%)} = \frac{\frac{\text{molH}_2(\text{GC})}{\text{molCO}_2(\text{GC})}}{\frac{\text{molH}_2(\text{theoretical})}{\text{molCO}_2(\text{theoretical})}} \quad \text{Eq.3}$$

$$\text{Carbon to gas (\%)} = \frac{\text{mgC}_{\text{gas}}}{\text{mgC}_{\text{i(theoretical)}}} \quad \text{Eq. 4}$$

Result and discussion

Early batch experiments were conducted with 1 wt. % ethanol in 75 mL distilled water at 230 °C, 28 bar, with 0.2 g of each of the four catalysts for 2 h. The ethanol APR reaction is showed in the following equation:



The highest ethanol conversion at 2-hour reaction was 72 % for Ru/Al₂O₃ catalysts (Fig. 1a), while it showed the lowest APR H₂ selectivity (Fig. 1b), which gives an indication on the extent of APR reaction respect to side-reactions.

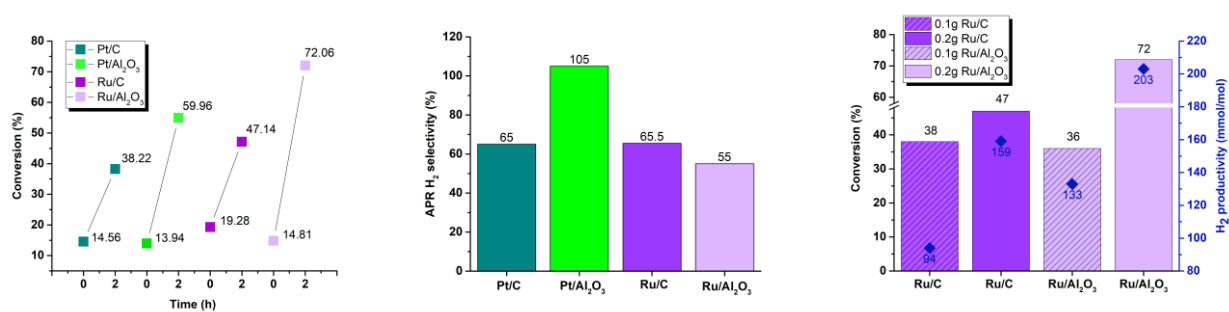


Fig. 1: The ethanol conversion in a 2-hours batch experiment (a), the APR H₂ selectivity (b) for the four tested catalysts. 2-hour ethanol conversion and H₂ productivity of 0.1g and 0.2g of Ru-based catalysts (c).

Whereas, giving a look to the gas distribution, the Ru/Al₂O₃ catalytic test showed the highest H₂ molecular content, accounting to 200 mmol of H₂ per mol of carbon in the feedstock, at the end of the reaction. Considering the lower molecular weight of Ru (101 g/mol) respect to Pt one (195 g/mol), APR tests were repeated by reducing the Ru catalyst content by half to achieve an equal theoretical number of moles for the two active metals. As shown in Fig. 1c, Ru/Al₂O₃ exhibits a 50% reduction in ethanol conversion compared to its counterpart at 0.2 g, whereas the decrease in H₂ productivity is less pronounced, accounting to only 34 %. Differently happens to Ru/C catalysts showing only a 20 % reduced ethanol conversion compared to their 0.2 g equivalent. Additional analysis for catalyst characterization should explore the distribution of the active phase on the support surface and the size of metal particles to elucidate the distinct behavior of the two Ru-based catalysts. Testing three ethanol starting concentrations (0.5%, 1%, and 1.5% wt.) under unchanged operative conditions revealed that the optimal ethanol conversion occurred at the lower concentration, which is promising for wastewater valorization.

Conclusion

Preliminary APR tests showed encouraging results in terms of H₂ productivity compared to literature works, leaving plenty of room for system optimization. Catalyst to ethanol ratio demonstrated to have an impact on the overall APR performance, thus a structure sensitivity analysis of the catalysts urges to be done, aiming to explain the effect of the metal-support selection on the ethanol conversion and H₂ selectivity. In the view of wastewater valorization, real streams composition will be addressed in order to investigate the impact of salinity, pH and the presence of other compound to the APR performance in the view of scaling up the technology.

Acknowledgments

This Project is funded by the European Union – NextGeneratonEU - PNRR-NGEU -DM351/2022.

References

- [1] K. Khandelwal and A. K. Dalai, "Integration of hydrothermal gasification with biorefinery processes for efficient production of biofuels and biochemicals," *Int. J. Hydrogen Energy*, vol. 49, no. PA, pp. 577–592, 2023, doi: 10.1016/j.ijhydene.2023.10.337.
- [2] G. Zoppi, G. Pipitone, R. Pirone, and S. Bensaid, "Aqueous phase reforming process for the valorization of wastewater streams: Application to different industrial scenarios," *Catal. Today*, vol. 387, pp. 224–236, 2022, doi: 10.1016/j.cattod.2021.06.002.
- [3] L. G. Seluy and M. A. Isla, "A process to treat high-strength brewery wastewater via ethanol recovery and vinasse fermentation," *Ind. Eng. Chem. Res.*, vol. 53, no. 44, pp. 17043–17050, 2014, doi: 10.1021/ie500438j.
- [4] A. N. Joshi and P. D. Vaidya, "Recent studies on aqueous-phase reforming: Catalysts, reactors, hybrid processes and techno-economic analysis," *Int. J. Hydrogen Energy*, no. xxxx, 2023, doi: 10.1016/j.ijhydene.2023.06.314.