ABSTRACT

With global energy demand reaching 620 EJ and 53.2 Gt CO_2-eq. emissions in 2024, 74.5% of which is attributed to the use of fossil fuels, the need to accelerate the shift toward renewable energy systems is more urgent than ever. In this context, biorefinery technologies, particularly aqueous phase reforming (APR), offer a promising route for producing H_2 from biomass-derived wastewaters, contributing to energy recovery strategies. APR is a thermo-catalytic process for converting oxygenated hydrocarbon into a H_2-rich gas mixture, under moderate temperatures (200–270 °C) and pressures (15–60 bar). However, the industrial application of wastewater-based APR remains limited by catalyst deactivation and economic challenges due to a relatively low technology readiness level and the limited scalability to different wastewaters. Experimental tests were performed on selected feedstocks of interest from both a compositional and a national strategic perspective, specifically pulp and paper (P&P) mill effluents and winery wastewaters (WWW). These results were combined with techno-economic (TEA), energy sustainability (ESA), and life-cycle assessments (LCA), aiming to bridge the gap between lab-scale results and process upscale for industry, outlining key technical, economic, and environmental challenges. Experimental results revealed that while P&P effluents exhibited low reactivity due to their dominance of poorly reformable acids and low pH, WWW showed strong potential as an APR feedstock, since over 70 wt.% of total organic carbon was ethanol. Therefore, a deep investigation of ethanol APR performances in varying operating conditions was carried out. Ethanol conversion reached 100% at 270 °C within 1 hour, compared to only 60% at 230 °C, with 250 °C providing the best trade-off between conversion and H_2 productivity. Among the commercial catalysts, Ru/Al_2O_3 showed higher conversion and H_2 productivity than Pt/Al_2O_3, although Pt offered slightly better H_2 selectivity. To reduce noble metal content, a 2 wt.% Ru/CeO_2 catalyst was synthesized via exsolution, a novelty in the field of APR. While exsolution was successfully obtained, its APR performance remained modest, likely due to limited surface area and large particle size. Further tests with exsolved Ru- and Fe-based catalysts supported on yttria–zirconia revealed that the bimetallic 2 wt.% Ru–1 wt.% Fe system delivered the highest H_2 productivity, suggesting a beneficial Ru–Fe synergy and confirming the potential for reduced noble metal use without sacrificing activity.

Building upon these findings, process-scale simulations were developed for an industrial facility treating 2.5 m^3/h of WWW through two configurations: Scenario 1 (S1) for CHP generation, and Scenario 2 (S2) for H_2 purification and recovery. Energetic analyses confirmed that both systems were energetically self-sufficient, with Energy Sustainability Index (ESI) values above 1, indicating positive net energy generation. A similar trend was observed for the EROI, with values of 1.57 for S1 and of 2.71 for S2, further confirming long-term energy feasibility. Since both ESI and EROI remain only slightly above unity, this

highlights a limited operational margin; consequently, system sustainability relies heavily on efficient heat recovery and stable reaction performance to maintain the overall energy balance.

The minimum selling prices (MSPs) were 0.86 USD/kWh for S1 and 15.5 USD/kg H_2 for S2, both above current market levels, mainly due to the high capital costs of the APR reactor, CHP, and PSA units, but demonstrating to be completely energy self-sufficient. Cost-reduction strategies showed counterintuitive insights: increasing ethanol conversion to 95% raised the MSP for electricity by 7% due to higher heat demand but lowered the MSP for H_2 by 21% (to 12.3 USD/kg H_2) thanks to improved H_2 yields. Further decreases could be achieved by integrating additional ethanol-rich wastewaters from other processes, strengthening overall economic viability and the role of APR within wastewater valorisation frameworks. No financial subsidies from the Italian government were considered.

The LCA confirmed competitive results, with GWP reductions of 80% for S1 compared to most European electricity mixes and 79% for S2 relative to conventional steam methane reforming. When compared with renewable technologies, the GWP values for S1 and S2 were comparable with photovoltaic and electrolysis powered by solar energy respectively, with platinum usage accounting for up to 70% of total GWP. This underscores the necessity for efficient recovery of noble metal catalysts or the transition toward non-critical metals.

Overall, this work shows that APR can be integrated into large-scale wastewater treatment, achieving up to 99% COD removal while recovering renewable energy. It outlines a model for APR-based biorefineries that unite wastewater purification and green energy production, in line with the circular economy goals and contributing to UN SDGs 6 (clean water and sanitation) and 7 (affordable and clean energy).