H₂ production by aqueous phase reforming of brewery wastewater


Departamento de Ingeniería Química, C/Francisco Tomás y Valiente, 7, Universidad Autónoma de Madrid, 28049, Madrid, Spain
Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, 20500, Turku/Åbo, Finland
Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia

*e-mail: adriana.souzade@uam.es

Aqueous phase reforming (APR) is an attractive alternative for H₂ and alkanes production from biomass-derived compounds. Good results have been reported in literature for a variety of model compounds, however some studies have shown that the cost of the feedstock may be an important drawback for the application of APR. The use of APR could be extended to biomass-derived wastewater treatment, thus integrating wastewater treatment and valorisation of effluents. This new application could be of special interest in the case of industries that produce large volumes of wastewater with high organic loads, such as breweries and fruit juice industry, and/or for wastewaters that are difficult to treat by conventional technologies.

Brewery wastewater has a large potential for valorisation by APR taking into account that the brewing industry generates large volumes of wastewaters (3-10 L wastewater/L beer) with a high organic load (2000-32500 mg/L of chemical oxygen demand (COD)). In this work, brewery wastewater was treated by APR with the focus mainly in H₂ production. The effect of some process parameters, such as reaction temperature, organic load and addition of bases on the catalytic performance was investigated. The experiments were conducted in batch and continuous reactors using Pt and Pt based bimetallic (PtRe and PtPd) catalysts and the support effect was evaluated using different carbon materials. Likewise, the catalysts stability was investigated and hydrogenation was performed as a pre-treatment of APR with the objective to increase the H₂ production and reduce the formation of carbonaceous deposits. The best catalytic performance was observed at higher temperature (220 °C) for catalysts supported on highly mesoporous carbon blacks with virtually no microporosity and high pH slurry (≈ 50 % of H₂ and 12.2 mmol H₂/g COD). At the lowest wastewater organic load, a high organic carbon removal was achieved (up 99 %) and H₂ yield increased to 15.4 mmol H₂/g COD, H₂ yield increased by addition of KOH to wastewater. Increasing KOH concentration led to CO₂ free H₂ without significant changes in H₂ yield. In continuous APR the catalysts showed some deactivation with time-on-stream, due to the coke deposition on the catalyst surface. The pretreatment of wastewater by hydrogenation improved H₂ production in the subsequent APR processing avoided reaction routes favouring the formation of solid carbonaceous deposits that lead to higher catalyst deactivation. In addition, the combined hydrogenation-APR process was considered efficient since H₂ production compensated for the consumption in hydrogenation, and moreover increased the catalyst durability.

In additional case studies, the APR of fish canning wastewater resulted in high organic carbon removal (45-60 %), however the total of gas produced was low in all experiments, due to the presence of salts that lead to catalyst deactivation. In the APR of fruit juice wastewater, H₂ production was around 6.6 mmol H₂ per g COD in the pH range tested (2-12), and a decreased of H₂ yield was observed at high salinity due to catalyst deactivation.

Keywords
Biohydrogen, aqueous phase reforming, brewery wastewater.