CARBON-SUPPORTED Pt CATALYSTS FOR THE TREATMENT AND VALORISATION OF BREWERY WASTEWATER THROUGH AQUEOUS PHASE REFORMING IN ALKALINE MEDIUM

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Introduction

Cortright *et al.*[1], in their pioneer work, showed that H_2 and alkanes can be produced with both high selectivity and yield from organic oxygenated compounds by aqueous phase reforming (APR) under mild reaction conditions (473–523 K, 15–50 bar) using supported metal catalysts. Since then, many studies have been carried out dealing with the conversion of different organic compounds, mainly for H_2 production. Some concerns have been raised on the feasibility of APR when it is targeted to the conversion of organic compounds with commercial value[2].

The current work showcases our project on the extension of APR to the treatment of biomass-derived wastewater, thus integrating wastewater treatment and valorisation of residues. Since a waste is used as substrate for the production of H_2 and alkanes, this approach overcomes the limitations of the process related to the use of substances with commercial value. Food and beverage industries producing large volumes of wastewater with high loads of biomass-derived organic compounds, such as brewing plants, are interesting candidates for the implementation of wastewater treatment by APR[3]. Basicity of wastewater is a key factor regarding the application of APR to wastewater, because cleaning-in-place (CIP) operations commonly used in this type industries lead to wastewaters with basic pH due to the use of bases (KOH, NaOH) in the CIP sequences, and the role of these bases in the APR reaction has not been well addressed.

The case study is based in the use of Pt catalysts using different carbon materials as supports for the treatment and valorisation of brewery wastewater through APR. The effects of support type and the basicity of the effluent on the process performance was analysed. Likewise, a real brewery wastewater has been tested to learn on the potential of application APR to these effluents. The stability of mono and bimetallic catalysts were evaluated, and finally energetic integration of the process was assessed by simulation.

Materials and Methods

3%Pt/C catalysts were prepared by incipient wetness impregnation using two commercial activated carbons (CAP and MER), three carbon blacks (ENS250, ENS350 and KJB) and mesoporous graphitized carbon black (C-MESO) as supports. 3%PtRe/C catalyst was prepared by sequential incipient wetness impregnation with a metal ratio of 1:1, 1:2 and 2:1 using MER as support. The supports and catalysts were characterized by N_2 adsorption-desorption, pH slurry and STEM.

Synthetic and real brewery wastewater were used as substrates. Synthetic brewery wastewater (SBW) was prepared based on typical composition found in brewery wastewater according to literature[4]. Real brewery wastewater (RBW) was collected from the plant of an international brewing company based nearby Madrid (Spain). In order to analyse the effect of pH on the catalysts performance NaOH and KOH were added to adjust the pH of SBW to the same pH as real brewery wastewater (RBW). Likewise, the effect of the base concentration was evaluated using KOH. RBW showed TOC and COD values of 1646 and 4674 mg/L, respectively and basic pH (pH 11). SBW was prepared with a TOC and COD of 1871 and 5846 mg/L, respectively.

The study of the effect of support and the basicity of the effluent was performed in stainless steel batch reactors at 493-498 K and 24-28 bar during 4 h, using 0.3 g of Pt/C catalysts in 15 mL of reaction volume under Ar atmosphere. The catalysts deactivation study was performed in a continuous fixed bed reactor over Pt/C and PtRe/C at 498 K and 28 bar, varying the weight hour space velocity (WHSV) and the Ar flow. The catalyst (1 g) was placed into a trickle bed reactor and the SBW (pH adjusted to 10) was introduced to the reactor by a HPLC pump. The gas phase was analysed by a GC/FID/TCD. The final effluents were characterized by TOC and COD measurement.

Simulation of the APR was performed using software Aspen HYSYS v10 in order to assess energetic sustainability and estimate costs. Mass and heat balances were calculated using experimental data and estimations. Sensibility studies of selectivity to H_2 and alkanes vs wastewater concentration were carried out. Sorbitol was used in the simulation as model contaminant as it has a C, H and O content similar to the average of the organic compounds in the wastewater.

Results and Discussion
Supports and catalysts characterization
The carbon black supports (ENS250, C-MESO, ENS350 and KJB CAP) showed slightly basic or basic pH slurry and did not present significant micropore volume (< 0.001 cm^3/g), except ENS350, which presented a small contribution of micropore (0.12 cm^3/g). The activated carbons MER and CAP yielded basic and acidic pH slurry, respectively, and a significant contribution of micropore volume (0.38-0.48 cm^3/g). Impregnation of metals did not produce any significant variation of the porous texture and pH slurry. The mean NPs size for all the metal catalysts was quite similar, in the 3.7-4.7 nm range, except in the case of Pt/KJB and PtRe(1:1)/MER, which showed smaller value of mean NPs size (2.3 and 1.6 nm, respectively).

Effect of the support on catalysts performance
The effect of the support on the catalysts performance in the APR of SBW was investigated in batch experiments at 498 K and 24-28 bar using Pt/CAP, Pt/ ENS250, Pt/ENS350 and Pt/C-MESO as catalysts. Blank experiments (without catalysts) resulted in TOC and COD removal values between 48-54 %, which can be partly ascribed to hydrothermal carbonization (HTC). The TOC and COD removal was improved to ca. 80% in catalysed ones, particularly for Pt/CAP, Pt/ENS250 and Pt/ENS350 catalysts. Removal above 95% was achieved by increasing catalyst load.
Blank experiments produced a very low gas volume (2.2-3.3 mL), consisting mainly of CO_2, essentially ascribed to HTC. Catalysed APR increased substantially the volume of gas produced (15.3-56.1 mL) with high percentage of valuable gases, H_2 and alkanes (41.7-71.6 %). Pt/ENS250 yielded the highest gas volume (56.1 mL), carbon conversion to gas (*CC gas*, 50.0%) and H_2

percentage in the gas fraction (48.9%), attributed to both the moderate basic character of the support and its mesoporous texture.

The maximum H_2 yield (Y_{H2}) values obtained with Pt/ENS250 (12.2 mmol H_2/g COD_i , i.e. $\approx$ 293.9 mL H_2/g COD_i) were higher than those reported in the literature[5] for the anaerobic biological treatment of an equivalent brewery wastewater (initial COD ca. 6000 mg/L, 149.6 mL H_2/g COD), thus showing the potential of APR as way of valorization of brewery wastewater. The yield to the sum of H_2 and CH_4 was also higher than for typical anaerobic biological treatment.

Effect of basicity of wastewater on catalysts performance

The effect of NaOH and KOH concentration on the catalysts performance in APR of SBW was analysed in batch experiments with different 3%Pt/C catalysts (Pt/ENS250, Pt/KJB, Pt/MER and Pt/CAP) at 493 K and 24-28 bar. Likewise, a RBW was tested.

The lowest TOC and COD removal (40-60%) corresponded to the blank and can be ascribed mostly to HTC of the organic substrates. In general, the TOC and COD removal were higher when catalysts were used, particularly in the case of Pt/KJB, Pt/MER and Pt/CAP, which reached removal values close to 70%. The addition of KOH and NaOH to SBW did not provoke relevant changes in TOC and COD removal. No significant differences in TOC and COD removal were found by using NaOH or KOH in the experiments with SBW.

The catalysts supported on carbon blacks showed a lower *CC gas* and Y_{H2} than those supported on activated carbon. The addition of bases led to lower percentages of CO_2 in the gas fraction with all the catalysts tested, particularly in the experiments with SBW+KOH, indicating that the addition of a base was effective for the removal of CO_2. However, Y_{H2} was higher only with the Pt/KJB catalyst, possibly due to the base addition favoured the base-catalysed dehydration reactions followed by hydrogenation that reduces the H_2 production.

Comparing the bases used, the highest percentage of H_2 was obtained with KOH. Pt/ENS250 catalyst gave the highest percentage of valuable gases in the gas fraction ($\sim$75%) and Y_{H2} (8.9 mmol H_2/g COD_i $\approx$ 213.6 mL H_2/g COD_i) with SBW+KOH. Given the good results obtained with the Pt/ENS250 catalyst, it was selected to assess the effect of the initial pH (pH_i) in the APR of SBW+KOH. The pH_i values tested (11, 13.0 and 13.5) were selected taking into account the previous results of CO_2, thus providing the sub- and over-stoichiometric amount of KOH needed to convert all the CO_2 produced to K_2CO_3.

Around 70% of TOC and COD removal was reached at pH_i 11, while lower removal was achieved at higher pH_i, showing that pH influences reaction pathway, increasing the production of liquids without increasing significantly the H_2 yield. This may be due to competitive reactions involving base-catalysed dehydration followed by subsequent hydrogenation. *CC gas* significantly decreased from around 32%, for a pH_i of 11, to around 15% for pH_i of 13 and 13.5, due to the in-situ removal of the CO_2 giving rise to K_2CO_3. Y_{H2} did not change significantly with the initial pH of the wastewater (8.7-9.0 mmol H_2/g COD_i). The amount of alkanes was similar in all the experiments (0.31-0.34 mmol), however, the addition of KOH reduced the formation of C_2^+, probably because the dehydration-hydrogenation of alcohols is hindered.

The study of the treatment by APR of RBW was carried out at the pH_i of the water produced in the brewing plant (11). The removal of TOC and COD upon APR of RBW ranged between 22-75% and 30-78%, respectively. The lowest values corresponded to the blank, which provokes

mainly provokes HTC at a lower extent than for SBW. The removal of TOC and COD from SBW and RBW was equivalent with Pt/ENS and Pt/KJB, whereas and slightly lower removal was achieved with Pt/MER.

Carbon black-supported catalysts (Pt/ENS and Pt/KJB) yielded *CC gas* between 27 and 40%, significantly higher than that obtained with Pt/MER. Y_{H2} with the Pt/KJB catalyst reached 12.9 mmol H_2/g COD_i ($\approx$ 309.1 mL H_2/g COD_i).

Catalytic stability study

In all the continuous experiments, deactivation of the catalysts was observed after a time-on-stream of 2-4 hours, however the catalysts showed stable behaviour during 24 after the initial deactivation. The effect of H_2 stripping on the catalytic stability was evaluated by increasing the Ar flow from 5 to 40 mL/min using Pt/MER catalysts at a flow rate of SBW of 1 ml/min. TOC removal changed significantly with time-on-stream (TOS), mainly at low Ar flows (5 and 20 mL/min). At the highest Ar flow (40 mL/min) the catalyst remained more active in TOC removal and H_2 production was improved. This can be interpreted in terms of striping of H_2 caused by higher Ar flow, thus decreasing the availability of H_2 for secondary reactions on the catalysts surface. Bimetallic catalysts presented higher H_2 production rate than monometallic Pt/MER, with PtRe(1:1)/MER showing the highest H_2 production rate (Figure 1).
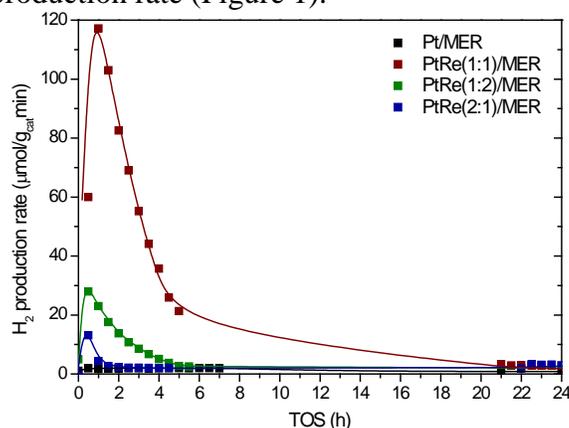

Figure 1. H_2 production rate by monometallic and bimetallic catalysts *vs* time-on-stream in the APR of SBW (498 K, 28 bar, 1 mL/min SBW flow, WHSV = 0.12h^{-1}, 40mL/min Ar flow).

The catalysts stability study also was performed varying the WHSV in the 0.03-0.48 h^{-1} range (basis: 0.2% C wt. in SBW) using PtRe(1:2)/MER catalyst. TOC removal was found to decrease with increasing WHSV. The carbon content in the liquid phase increased with an increase of WHSV due to shorter contact times. *CC gas* and Y_{H2} also decreased with an increase in WHSV, accordingly. In contrast, at higher WHSV the percentage of H_2 in the gas fraction was higher. At higher space velocities, the contact time of the feed and the catalyst is lower. Therefore, reactions that consume H_2 contribute to a lesser extent and a higher percentage of H_2 is observed in the gas.

Simulation of APR of brewery wastewater: energetic integration

The experimental results above reveal that APR is an interesting alternative enabling removal of organic contaminants and simultaneous conversion of contaminants to valuable gases. However, the operating conditions needed makes the process energy demanding. A sensibility analysis was carried out by simulation to assess the self-sustainability of the process. The results showed that

the process can be energy self-sustained, and in addition generate an excess of energy that could be exported, as long as the concentration of the organic contaminants is above ca 0.8-1%. The excess of pressure above water vapor pressure is relevant not only to favour water gas shift reaction, but also to minimize water vaporization to the gas phase and thus the consumption of enthalpy by the reactor. The energy balance was also very sensitive to the selectivity of the reaction. The shift of selectivity to H_2 production increases the consumption of enthalpy in the reactor, which demanded a heat input thus decreasing the overall excess of heat. Therefore, selectivity to alkanes can be an attractive option if H_2 is not marketed and the valuable gases are burned or feed to engines or gas turbines.

Applicability to other types of wastewater
Industries that produce large volumes of wastewater with high loads of organic compounds derived from biomass can be considered interesting candidates for the implementation of wastewater treatment by APR. In addition to brewery wastewater, in our project we have studied other types of wastewaters such as tuna cooking, fruit-juice and coke plant wastewater. The concept can be extended to a broad variety of wastewaters, although salinity can be a limiting factor, as it was found in the case of tuna cooking wastewater.

Conclusions
Aqueous phase reforming (APR) of brewery wastewater has been shown as an alternative to conventional water treatment schemes. APR can combine effective removal of the pollutants (>95%) with conversion of the contaminants to valuable gases, mainly H_2 and alkanes (12.2 mmol H_2/g COD_i). The applicability has been proved for both synthetic and real wastewater. The basicity of brewery wastewater, due to the bases used in the cleaning-in-place systems, only has a minor influence in the removal of TOC and COD, whereas it leads to higher percentage of H_2 and alkanes in the gas produced due to in-situ CO_2 capture. Deactivation is a concern for application, but strategies such as the use of bimetallic catalysts and carrier gas can help to minimize it. Simulation showed that the gas produced can provide the heat input required by the process together with an excess of heat that can be exported.

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