**Sustainable hydrogen production from corn stover hydrothermal liquefaction aqueous phase**

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**1. Introduction**

The hydrothermal liquefaction (HTL) has the aim of producing liquid biofuels starting from wet biomass [1]. In this scenario, the aqueous phase by-product stream (HTL-AP) needs a suitable treatment/valorization, because it can dissolve up to half of the carbon initially present in the feedstock, depending on the reaction conditions [2]. Therefore, its exploitation is a critical achievement for the commercial implementation of this process. Herein, we investigated the aqueous phase reforming as a possible strategy to reach this goal.

Aqueous phase reforming (APR) has been proposed in the pioneering work of Dumesic’s research group for the production of H2 from biomass-derived compounds under milder reaction conditions (220-270 °C, 30-60 bar) compared to conventional fossil-based steam reforming [3]. Most of the research focused on single-compound solutions, which were fundamental for the sake of comprehension of the catalyst structure-activity relationship and the influence of operating conditions. However, there is a lack of information on the catalytic behaviour when multi-components solutions are evaluated. As a matter of fact, the real streams present in industrially relevant environments are constituted by multiple species, belonging to several different classes of compounds (carboxylic acids, alcohols, hydroxyacids, ketones, aromatics, amides, etc.) [4]. In this work, APR was studied to exploit this strategic by-product and obtain a hydrogen-rich gas phase, which can be further used for the hydrotreatment (i.e., deoxygenation) of the biocrude. The corn stover HTL-AP was considered as model feedstock, due to the abundance of this lignocellulosic residue. Glycolic, acetic and propionic acid as individual acids and in combination were tested over different catalysts (5% Pt/C, 5% Pt/γ-Al2O3 and 5% Pd/C) to investigate to which extent the presence of one molecule affected the reactivity of the other one. Furthermore, the kinetic of glycolic acid was evaluated on 5% Pt/C.

**2. Methods**

The APR reactions were performed in a 300 mL 4560 series mini benchtop reactor (Parr). In a typical reaction, 75 mL of solution and 0.15 g of catalyst (commercial, powder form) were used, with the desired concentration of glycolic, acetic or lactic acid. Once fastened, the reactor was purged with nitrogen to remove atmospheric oxygen, finally pressurized at 0.3 MPa with N2, and heated up to the desired temperature (250-270 °C). At the end of the reaction, the reactor was cooled down, the gas phase collected in a syringe and analysed by µGC, while the liquid phase was filtered to separate the catalyst and then analysed through HPLC.

**3. Results and discussion**

Firstly, the absence of external and internal mass transfer limitations was verified. Figure 1-left shows the results of the system constituted by acetic and glycolic acid with Pt/C catalyst. If acetic acid was the only compound in the solution (PtC-G0A1), its conversion was 23.7%. Adding glycolic acid in a 1:4 glycolic/acetic ratio (PtC-G0.25A1) dramatically reduced its conversion up to 2.4%. This outcome is significant of the strong adsorption of glycolic acid on the active metal compared to acetic acid. When glycolic-acetic acid ratio gradually increased up to 1:1 (PtC-G1A1), the final conversion of acetic was -8.1%. It means that eventually its concentration increased: this was attributed to the side reactions involving glycolic acid, which can be hydrogenated to acetic acid by removing its hydroxyl group. Being the evaluation of the actual conversion complicated by this side-reaction, an alternative approach can be followed by considering the methane production. In fact, it is scarcely produced by glycolic acid, while it is the main product (together with carbon dioxide) for acetic acid. Figure 1-left demonstrates that a slight production of methane was obtained also in the PtC-G1A1 test, but globally this conversion was wrapped by the higher production. A similar trend was reported also for Pt/Al2O3 and Pd/Al2O3 (data not shown). In particular, the Pd-based catalyst, due to the lower activity, reported both a negligible acetic acid activation and formation, reaching higher hydrogen selectivity. The strong adsorption of glycolic acid was confirmed by the kinetic study, which highlighted the apparent zero-order reaction for this compound.

A similar approach was used for the acetic/propionic solution, and the result are displayed in Figure 1-right. Acetic acid conversion gradually decreased while propionic concentration increased in the feed; Despite this trend, the conversion was significantly higher than in the former binary solution. Since acetic acid was not significantly produced from propionic acid, the reported conversion may be considered as the real one, without considering the methane production. The study of these two binary mixtures allowed to derive a ranking in the adsorption of small biomass-derived oxygenates on platinum, being glycolic > propionic > acetic acid. The stronger adsorption of glycolic acid may be attributed to the presence of both a carboxylic and hydroxyl group, which favored the anchoring of the molecule on the platinum site. Further studies on this subject, in particular with the help of techniques such as density functional theory, could help to shed light on the adsorption path, and provide hints on the rational design of more effective heterogeneous catalysts.

 

**Figure 1.** Influence of solution composition on APR performance. Reaction conditions: 75 mL solution, 270 °C, 0.15 g 5% Pt/C, 1 h.

**4. Conclusions**

APR of a model corn stover HTL-AP was performed to derive information on competitive adsorption phenomena. Glycolic, acetic and propionic acid were investigated alone and in mixtures to get an insight on their reactivities with different catalysts, the affinities with the active sites and the relative influences between the molecules. The full characterization of both liquid and gaseous products showed that acetic acid conversion was more influenced by the presence of glycolic acid rather than propionic acid. The insights gained from this work into the competition issues for the APR of complex mixtures can prompt future research in the design of catalysts for carboxylic acid activation, tackling the challenge of zero-waste biorefineries.

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