**ION EXCHANGE RESINS: AN ALTERNATIVE FOR THE REMOVAL OF PHENOLIC COMPOUNDS FROM BREWER’S SPENT GRAIN**

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**Highlights**

* Use of anionic ion exchange resin to remove phenolic compounds
* High efficiencies on the removal of both p-coumaric and ferulic acids in the pretreatment liquid and enzymatic hydrolisates
* Low sugar losses for both the pretreatment liquid and enzymatic hydrolisates

**1. Introduction**

The use of lignocellulosic biomass as a feedstock for biofuels production is still challenging due to the formation of toxic products in the pretreatment that are inhibitory to fermentation and hence may affect economics. The type and concentration of inhibitors formed depend on the pretreatment technologies, being aliphatic carboxylic acids (e.g. acetic, formic, levulinic acid), phenylic compounds (benzoic acid, phenolic compounds), furans (furfural and hydroxymethylfurfural) and uronic acids (galacturonic and glucuronic acid) the main by-products formed [1]. The presence of inhibitors in the hydrolysates play a vital role in ABE fermentation as they affect negatively fermentation yield and efficiency mainly due to its toxicity to microorganisms. Phenolic compounds including ferulic acid, p-coumaric acid, 4-hydroxybenzoic acid, vanillic acid, and vanillin can cause growth inhibition of *C. beijerinkii* and no butanol production. The presence of phenolic compounds inhibited ABE fermentation at concentrations as low as 0.5 g/L for gallic acid and 0.1 g/L for catechin [2].

To overcome the problem due to the presence of inhibitors, a detoxification step before fermentation is usually carried out. Removal of phenolic compounds involves techniques such as physical methods (evaporation, membrane separations, electrochemical detoxification), chemical methods (neutralization, overliming with calcium hydroxide, addition of reducing agents), liquid-solid extraction (activated carbon treatment, ion exchange resins) and biological detoxification by enzymatic catalysis mainly with the use of laccase and peroxidase [3-5]. The use of ion-exchange resins is also a promising detoxifying technology, due to the selectivity of the resins, which are able to remove practically the totality of the phenolic compounds present with very little losses of monosaccharides

Different anionic exchange resins have been tested and operating conditions were optimized with the objective of removing the inhibitors formed during the pretreatment of brewer´s spent grain before ABE fermentation step with minimum sugar losses.

**2. Methods**

Model solutions were prepared simulating sugar concentrations of pretreatment liquid obtained during acid diluted pretreatment of brewer´s spent grain (15% dry matter content, 121ºC, 30 min) and enzymatic hydrolysates from pretreated solid (15% solids loadings, 15 FPU/gDM Cellic CTec 2, 48h, pH 4.8). Major phenolic compounds founded in these liquids are p-cumaric acid and ferulic acid and concentrations tested were in the range 0.5-2 g/L. Four different commercial ion-exchange resins (Lewatit Monoplus MP500, Lewatit VPOC, Lewatit S4528 and Lewatit A365) have been tested, operating in batch mode, at solid/liquid ratios of 1%, 2% and 3% w/v. Temperature was maintained at 35ºC, pH of 5.0, 200 rpm and operating time was 24 h for all the experiments. The contents in sugars (glucose, xylose, and arabinose) and phenolics inhibitors were determined by HPLC [6].

**3. Results and discussion**

A different behavior on the sugar losses and inhibitor´s removal have been found when the pretreatment liquid was detoxified with ion exchange resins. The highest sugar losses (17-21%) were obtained when the resin Lewatit A365 (weak anion exchange resin) was employed and sugar losses increased when resin:liquid ratio increased. On the opposite, the resin Lewatit Monoplus MP500 (strong anion exchange resin) showed the lowest sugar losses (7.8-8.0%) and no influence was observed with resin:liquid ratio. Related with the removal of phenolic compounds, weak anion resins removed almost completely p-cumaric and ferulic acids even at 1% w/v resin:liquid ratio, whereas when strong resins have been tested, it is necessary to work with a 3%w/w resin:liquid ratio to attain phenolic compounds removal higher than 90.0%.

When the enzymatic hydrolysates were detoxified with anion exchange resins, phenolic compounds were completely removed due, mainly due to the lower concentrations founded in these streams. Related with monosaccharides, significantly sugar losses up to 24% have been obtained for both weak and strong resins.

**4. Conclusions**

Weak anionic resins allow to remove almost completely phenolic compounds from BSG hydrolysates (pretreatment liquid and enzymatic hydrolysates) with relatively high sugar losses. On the contrary, the operation with strong anionic resins lead low sugar losses and phenolic´s removal up to 90%. Further research will be focused on the column operation and optimization of the main parameters (bed volume/h, temperature, time of cycle and regeneration conditions) will be studied.

**References**

1. Jönsson and Martín, 2016. Bioresource Technology 199, 103–112.
2. Bellido et al. 2018. Food and Bioproducts Processing 108, 117-125.
3. Jönsson et al., 2013. Biotechnology for Biofuels 2013, 6-16.
4. Lee et al., 2015a. Process Biochemistry 50, 630-635.
5. Lee et al., 2015b. Bioresource Technolology 187, 228-234
6. Plaza et al., 2017. Bioresource Technology 244, 166–174