A techno-economic comparison between technologies for biomass fractionation including liquor re-use

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Introduction

The pre-treatment is a key step in the lignocellulosic biomass (LCB) preparation for hydrolysis and sugar conversion into fuels and chemicals. All the pre-treatments modify the structure and chemical composition of the LCB in order to improve the accessibility of cellulolytic enzymes that selectively convert the cellulose into glucose. Several pre-treatment methods have been employed, being steam explosion, dilute acid hydrolysis and water-solvent fractionation the more used (Pandiyan et al., 2018). In previous work (Vergara et al., 2018) LCB fractionation with an ethanol-water (EW) mixture has been proposed as a possible alternative to the more common diluted sulfuric acid (DSA) pre-treatment. By varying the experimental conditions of the EW fractionation, it has been demonstrated that this LCB pre-treatment favourably competes with acid hydrolyzed biomass and a high yield in free sugars could be obtained from the enzymatic hydrolysis (EH) of the pulps with a low-moderate energy input. The main drawback of pre-treatments is the associated costs of energy and product concentration stages: In the case of the water-solvent fractionation they increase with the additional energy involved in the solvent recovery. This issue is a bottleneck for the development of a cost effective bioprocess which results in increased downstream processing cost, when compared with crude oil alternative (Kalafatakis et al., 2017). Although EW pre-treatment is, apparently, the less favourable pre-treatment in terms of energy consumption (Kautto et al., 2014), it is more efficient in the delignification than diluted acid pre-treatments. Moreover, EW pulps exhibit less inhibition problems in the further saccharification and fermentation stages (Palmqvist and Hahn-Hägerdal, 2000).

The cost derived from the solvent recovery is an important drawback and some authors have found the process to be not efficient, for example in the simulation of the ethanol production from hardwoods. Kautto et al. (2014) used the organosolv pre-treatment and determined that, comparing with the diluted acid pre-treatment, this pre-treatment need 34% more energy, provoking the overall process to be not energy self-sufficient. Rodrigues Gurgel da Silva et al. (2017) compared ethanol production from spurce chips using EW and DSA pre-treatment and found that total annual cost is almost 50% more expensive with EW than DSA pre-treatment.

Diverse efforts have been made to address this problem. The more common approach is the use of a minimum liquid/solid (L/S) ratio during the pre-treatment, which allows reducing the size of the equipment, as well as saving energy in solvent recovery and pumping (Zhu and Pan, 2010). However, this solution is not always possible because, at low L/S ratios, the contact between biomass and liquor is not enough to assure a good biomass fractionation. The problem is more relevant for herbaceous biomass than for wood chips, which need, approximately, L/S ratios of 20 L/kg and 10 L/kg, respectively.

Another possibility is to re-use the spent liquor as cooking liquor for successive treatments, by feed-backing a fraction of the spent liquor. This possibility has been used in the pulp industry to make the cooking stage more selective. The ethanol water re-use strategy (EWR) minimizes water and chemicals consumption, the amount of wastewater and energy expenditure, improving the environmental sustainability of the process. However, it leads to an accumulation of substances in the process, which can negatively affect subsequent stages.

In Vergara et al., 2019, liquor re-use in wheat straw fractionation with ethanol-water has been experimentally studied. The liquors obtained in six successive fractioning operations have been analysed. Results revealed that the number of re-uses reduces solids recovery (from 52.2 to 42.6%) and cellulose recovery (from 28.1 to 23.3%) with minor or no effect on the hemicelluloses and lignin removal. The more remarkable effect is an increase of the glucose yield (from 76.7 to 95.3% after enzymatic hydrolysis during 72 h).

In the present work, set up of EW, EWR and DSA fractionation process flowsheets are presented, and experimental data for EW and EWR from Vergara et al, 2019 is used for conducting an economic comparison of the fractionation process. The traditional DSA method was considered as a reference.

Material and methods

A simulation of the processes was designed in Aspen Plus v9.0 to set up a plant processing 100 ton per

hour of dry wheat straw. The biomass composition is described in Vergara et al, 2019. The NRTL (non-random two-liquid) property method was used and components in Aspen data base were used. Experimental conditions for EW and EWR and yields were taken from Vergara et al, 2019. A 20 liquid to solid ratio was used for simulation according to the experience.

<u>Process set up</u> - The simulated EW process considers the fractionation of biomass into a cellulose-rich solid fraction, precipitated lignin and a hemicellulose-rich concentrated liquid stream. The solid fraction is conducted to a two-step washing, and then conducted to an enzymatic hydrolysis process. The resulting product is a glucose solution. The further transformation of glucose is not considered, as the aim of this study is to compare fractionation processes. Ethanol from the spent liquor and from the first washing step is recuperated and recycled to the pre-treatment reactor. The resulting flowsheet is shown in Figure 1.-



Figure 1.- EW process flowsheet

Figure 2.- EWR partial process flowsheet

The re-use EWR implementation of pre-treatment and lignin precipitation is presented in Figure 2.-The conceptual scheme of re-use is challenging because of its dynamic nature. Implementation in Aspen plus software was conducted by considering six pre-treatment reactors. Each pre-treatment mass balance takes into account the experimental yields found in Vergara et al., 2019. The spent liquor of the n-1th reactor is conducted to the nth -reactor. The resulting liquid streams from washing steps are then mass-integrated. The complete EWR process scheme and DSA process flowsheet taken as a reference will be shown in the full paper.

Results and discussion

Utilities (almost hot utilities) of EW was found around 20 % more expensive than DSA, while operating costs were also higher. EWR allows to significantly reduce the utilities cost, and operating costs with the EWR alternative are similar to DSA. Make-up of ethanol is also significantly reduced in EWR than EW.

In the full version a detailed operating and investment costs will be presented and compared. A sensitivity analysis of liquid to solid ratio will be shown.

Conclusions

Re-use strategy significantly reduces energy, operating costs and water consumption of ethanol water fractionation process. The resulting EWR operating cost is similar to the reference diluted acid pre-treatment.

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