Analysis of catalyzed acid pretreatments as the basis for the design of lignocellulosic biorefineries

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Introduction

Lignocellulosic biomass has been described as the most abundant renewable source worldwide, where much of it is disposed of as waste on-site as a nutritional crop source or incinerated (Poveda-Giraldo & Cardona, 2020). The large availability and rich carbohydrate composition of lignocellulosic biomass have promoted extensive research for its valorization, especially in biorefinery processes. Cellulose is the most abundant renewable carbon source, which can produce different bioproducts such as fuels, food, and chemicals. However, cellulose is resistant to easy depolymerization or fractionation due to the high hydrogen bonding of its structure (Nishiyama, 2009), requiring harsh processing conditions that increase processing costs. Therefore, it is necessary to propose other conditioning mechanisms that allow the removal of other biomass fractions to valorize the cellulose easily. Different pretreatments have been proposed to hydrolyze lignocellulosic biomass, such as mechanical, thermal, chemical, and biochemical processes as well as combinations among them, which present advantages or disadvantages depending on their purpose. For example, thermal pretreatments demand high energy, mechanical pretreatments consume much time and electrical energy, and biochemical pretreatments present high residence times and operating costs regarding inputs such as enzymes. On the other hand, chemical pretreatments can effectively hydrolyze hemicellulose and partial lignin, increasing biodegradability rates in further cellulose conversions. Although acid hydrolysis can form compounds that are inbitorious for bioconversions, pretreatments with controlled conditions can overcome these drawbacks.

There are different acid pretreatments implemented for cellulose valorization. Acid hydrolysis has been shown to decrease cellulose crystallinity while removing hemicellulose and lignin heteropolymers (Pu et al., 2013). Organosolv has also been proposed for the solvation and solubilization of lignin as well as the degradation of five-carbon sugars, whose yields are improved when catalyzed with acids (Zhang et al., 2020). However, these pretreatments demand high costs for reagent recovery. Solid acids or heterogeneously catalyzed pretreatments have demonstrated degrees of recyclability in biotechnological processes (Joo et al., 2017). To date, no studies demonstrate the comparison of homogeneous and heterogeneous acid-catalyzed pretreatments as a preliminary step in biorefinery schemes. This work is focused on assessing, through techno-energetic, economic, and environmental aspects, pretreatment schemes as a design basis in biorefineries for the valorization of lignocellulosic biomass. Experimental and simulation data were used to compare dilute acid, organosolv and solid resin pretreatments.

Methodology

The acid pretreatments were compared in a high-pressure reactor (HP AutoLAB reactor E1823) using rice husks as raw material. For all pretreatments, a severity factor (Log (R_0)) equal to 3.75 was used for comparison. The dilute acid scheme involved an aqueous H_2SO_4 solution (2% vol.), while the organosolv, an ethanolic solution (50% vol.) acidified with 23 mM H_2SO_4. The dilute acid and organosolv pretreatments were carried out at 175°C and 150 rpm for 35 min and a feed ratio of 1:20 (mass:volume). On the other hand, the pretreatment with solid resin (Amberlyst 36) was carried out at 140°C for 4.25 h and 150 rpm. After the pretreatments, the hydrolysate was stored to characterize the content of sugars and degradation products by HPLC. On the other hand, the water-insoluble solid was washed with plenty of water to neutral pH and characterized in terms of cellulose, hemicellulose, and lignin based on international standards.

Based on the experimental results of the acid pretreatments, the schemes were scaled up considering the operating conditions, feed ratios, and lignocellulosic fraction removals. The pretreatments were simulated in Aspen plus v9.0 software (Aspen Technologies, Inc., USA), assuming a continuous rice husk flow of 50 tons d^{-1}. The economic analysis involved up-date parameters from Colombia. Meanwhile, the environmental assessment was carried out using the Waste Reduction Algorithm (WAR) software through eight environmental indicators.

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Results

As the main results, it was observed that the pH decreased at the end of the pretreatment time, which was to be expected since the addition of an acid catalyst, either homogeneous or heterogeneous, promotes the breaking of acetyl bonds of the hemicellulose structure for the formation of aliphatic acids, especially acetic acid. The

accumulation of these molecules increases the acidic character of the medium and promotes the degradation of oligomers and five-carbon monosaccharides to undesirable compounds such as furan-type furfural and hydroxymethylfurfural (HMF), which can be further transformed into levulinic acid and formic acid. Figure 1 shows the lignocellulosic composition of the water-insoluble solid in lignocellulosic terms. It was observed that hemicellulose was the macromolecule that was hydrolyzed the most in all pretreatments, decreasing its content compared to the original sample. Furthermore, it was observed that removals above 63% were achieved, where the dilute acid scheme was the most effective in hydrolyzing or removing hemicellulose. On the other hand, there were small alterations in terms of lignin removal for the dilute acid pretreatments and the acid resin, which was to be expected given the affinity and insolubility of lignin in acidic water, as opposed to the organosolv, which has ethanol in the medium. Approximately 50% lignin removal was achieved in the organosolv pretreatment. For all the pretreatments, removals higher than 12% were not achieved for cellulose since this polysaccharide has a high crystallinity and degree of polymerization due to the multiple hydrogen bonds, hindering its easy hydrolysis. This demonstrates the potential of acid catalyst-based pretreatments for preserving cellulose and its future use in bioconversion processes.

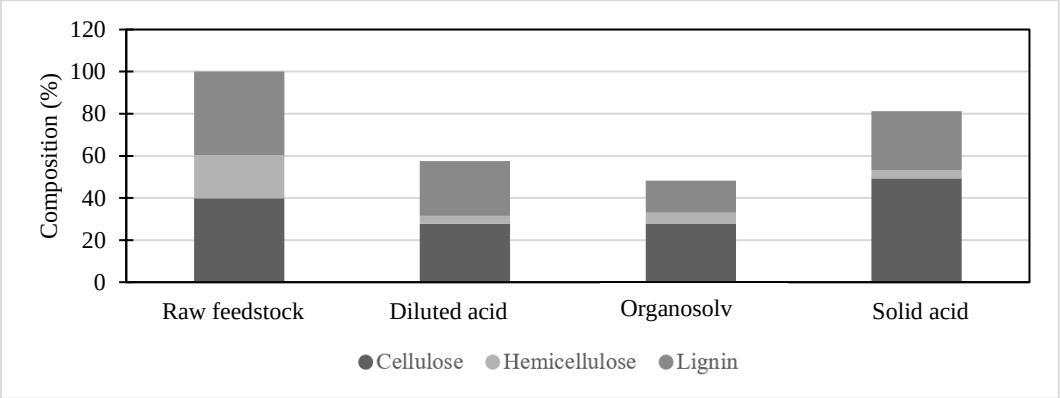

Figure 1. Lignocellulosic composition of rice husk after acid-catalyzed pretreatments.

Regarding the economic results, Table 1 summarizes some parameters calculated regarding investment (CapEx) and operating (OpEx) costs. It is possible to observe that the organosolv pretreatment is the most expensive investment since the solvent recovery stage was considered, involving processing units such as the distillation column, condenser, reboiler, reflux pump, and storage tank, among others. On the other hand, although the resin and dilute acid schemes have the same processing system of the mill, sieving, reactor, exchanger, and filter, the resin scheme is more expensive due to the size of the reactor, affected by the residence time of the 4.45h of reaction. Regarding operating costs, organosolv pretreatment has the highest values due to the additional need for service fluids such as cooling water and low-pressure steam from the distillation system or the use of ethanol and sulfuric acid in the reactive system.

Table 1. Summary of operating and investment costs at 50 ton d^{-1}.

Parameter	Pretreatment		
	Diluted acid	Organosolv	Solid acid
CapEx (M-USD)	0.94	3.26	1.64
OpEx (M-USD/year)	8.70	47.89	14.86
Raw material	1.74	29.3	8.06
Utilities	6.71	17.76	6.37
Maintenance	0.06	0.23	0.11

Conclusions

Acid-catalyzed pretreatments proved to be good schemes for removing hemicellulose and partial lignin for further cellulose valorization into bioproducts. Dilute acid pretreatment was shown to remove better five-carbon sugars, which can also be valorized and increase the economic profitability of biorefinery schemes. Despite working with highly corrosive compounds, dilute acid pretreatment demonstrates financial effectiveness in capital investment and operating cost. From the environmental perspective, there is no negative environmental impact in the evaluated schemes since the impact of the input streams is minimized compared to the output streams.

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