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Combination of Mechanical, Acid and Alkaline Pretreatments for Sugars Production from Corn Stover

Marcela Torres-León, Karina Ojeda-Delgado and Eduardo Sánchez-Tuirán

Chemical Engineering Program
Process Design and Biomass Usage Research Group
University of Cartagena, Campus Piedra Bolivar
Street 30 # 48-152. Cartagena, Colombia

Abstract

Biofuels from lignocellulosic biomass have the potential to reduce the fossil fuels consumption in the following years. However, the structure of these materials hinders degradation in the hydrolysis stage, which requires pretreatments that helps increase the production of fermentable sugars to obtain biofuel. Therefore, in this study three pretreatments were applied to corn stover biomass: Mechanical, with size reduction (0.5, 1, and 2 mm), followed by an alkaline pretreatment (NaOH 1.5% w/v) and subsequent acid pretreatment at different concentrations (H_2SO_4 2, 4, and 6% v/v). Finally an acid hydrolysis (1% H_2SO_4 v/v) of pretreated biomass was applied in order to evaluate the effect of different pretreatments in the amount of total reducing sugars (TRS).

Keywords: Lignocellulosic biomass, mechanical, alkaline, acid, pretreatment

1. Introduction

Ethanol is one of the biofuels that more contributes to the reduction of environmental pollutants generated by the use of fossil fuels [8]. Its production from lignocellulosic biomass is a complex process because these materials requires pretreatment stages to achieve a degree of delignification that does not obstruct the fermentation of the sugars [2, 12].

Several types of technologies have been proposed, among which four fundamental pretreatment techniques stands out: physical, chemical, physical-chemical, and biological [13]. Some authors have applied these techniques to different types of biomass such as corn stover in which there was a reduction in the lignin content by 70-85% and solubilization of 40-60% of the hemicellulose [7]. Other authors have implemented the combination of pretreatments applied to cane bagasse using diluted phosphoric acid, followed by a delignification with sodium hydroxide, yielding a production of 0.62 g of TRS / g of dry biomass with a yield of 99.59% by weight [6]. Therefore, the combination of pretreatments is a promising option for the degradation of biomass.

The mechanical pretreatments help to reduce the degree of polymerization and crystallization of the raw material but have low yields of glucose and xylose after hydrolysis; on the other hand, alkaline treatments eliminate lignin but does not solubilizes the hemicellulose contrary to the effect by the acids in the pretreatment [9]. Thus, the joint application of several pretreatments are recommended in some cases in order to increase its efficiency [9, 14].

Some authors have dedicated their studies to find the most efficient pretreatment techniques for certain types of biomass in obtaining TRS. Many of these pretreatments have being analyzed as possible routes for biofuels industry [1, 2, 3, 5]. In this work, the joint application of pretreatments to corn residues was made to analyze the degradation potential of this agroindustrial waste.

2. Materials and Methods

The corn stover consisting of stalk and leaf in a 50:50 weight ratio, was chosen as raw material. The material was previously separated and classified. The stems and leaves were selected and then dried.

2.1. Mechanical pretreatment

The reduction in the size of the biomass was made in order to increase the surface area per unit of mass. For this, the biomass was ground with a mill and sieved to take as samples the fractions of 2, 1, and 0.5 mm.

2.2. Alkaline pretreatment

For the alkaline pretreatment, a sample of 5 g of biomass was immersed in a 1.5% wt./v NaOH solution in a 1:13 solid-liquid ratio, for 2 hours at 100 ºC. After that, the solution was cooled down to room temperature and then filtered. The solid was washed with distilled water until neutral pH and then dried at 60°C for 2 hours. The pH for the liquid fraction was adjusted for the subsequent quantification of TRS by the DNS method [1].

2.3. Acid pretreatment

The dry biomass from the previous pretreatment was added in a solution of sulfuric acid in concentrations of 2, 4, and 6 % v/v in a ratio 1:30 solid-liquid at 75 °C for 90 minutes. After the operation time, the samples were filtered to separate the liquor and then sugars were measured with the DNS method. The solid material was washed until neutral pH and dried for 2 h at 60 °C [4].

2.4 Acid hydrolysis

The solid material from the pretreatments was mixed with a 1% v/v solution of H_2SO_4 in a solid-liquid ratio of 1:10. The mixture was heated in an autoclave at 121 °C for 1 h. Finally, it was cooled down to room temperature and filtered. Final sugars were quantified [3].

3. Results and Discussion

The content of cellulose, hemicellulose, and lignin present in the corn stover is shown in Table 1.

Table 1 Corn residues characterization

Fraction	**Stalks**	**Leaf**	**[11]**	**[10]**
Cellulose (%)	39.6	35.5	30.2 ± 2.6	36,4
Hemicellulose (%)	28.3	27.5	20.3 ± 2.3	22,6
Lignin (%)	8.0	3.3	15.4 ± 0.5	16,6
Ash (%)	0.52	4.9	N.R.	N.R.

*Corn stover residues

The results obtained show that corn residues have a potential carbohydrate source equal to 645.5 mg of sugars/g of dry material. The lignin content in corn leaves is relatively low, compared to the lignin content in the stems, which increases the resistance to chemical or enzymatic attack.

The biomass was milled, then alkaline pretreatment followed by pretreatment with diluted acid was applied according to the described methodology. Figures 1 and 2 shows the reducing sugars (RS) obtained in the liquid fraction from alkaline and acid pretreatment, respectively.

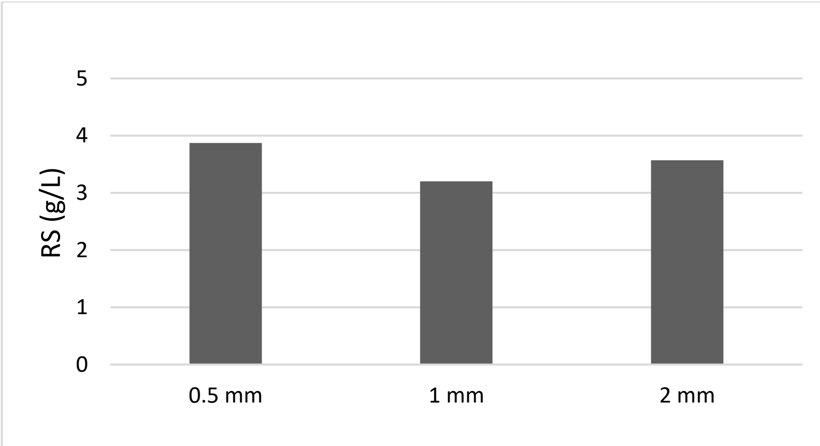

Figure 1. Average RS obtained after alkaline pretreatment for each particle size

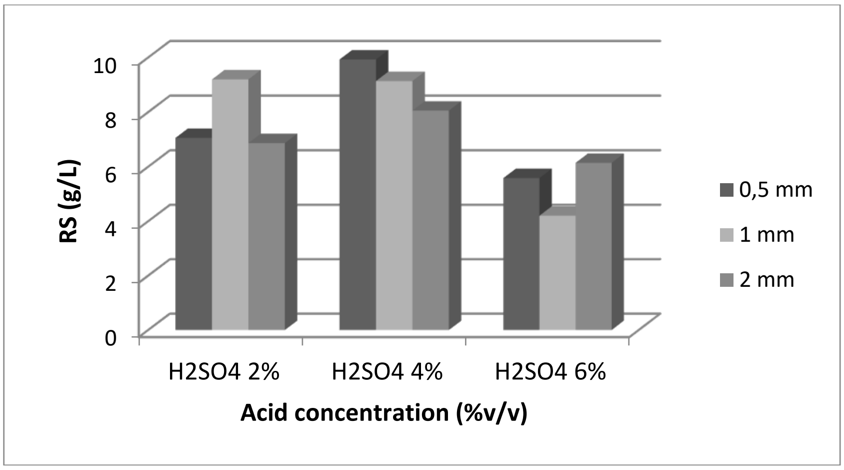

Figure 2. RS obtained after acid pretreatment for each particle size

The acid pretreatment yielded more sugars than the alkaline pretreatment, which is consistent with the objective of each pretreatment. The previous treatment with a base has the function of solubilizing the lignin. Also, the acid pretreatment hydrolyzed the hemicellulose present in biomass [3].

For the acid pretreatment, the previously alkaline treated samples were exposed to an acid pretreatment at three concentrations of H_2SO_4 (2, 4, and 6% v/v). The liquid product obtained was then filtered and pH adjusted. Finally, the sugars were quantified using the DNS method. Figure 3 presents the TRS from acid pretreatment. Results show that the pretreatment with H_2SO_4 at 4% v/v, reduced more sugars than others conditions. More severe pretreatments conditions caused other hydrolytic reactions that promotes the formation of inhibitory compounds [5]. Results showed that difference in carbohydrates degradation by reducing the particle size was not significant in pretreatment stages.

Table 2 shows the TRS for the process after all pretreatments and acid hydrolysis of the biomass. The concentration of TRS of the process decreases for higher acid concentration and lower particle size, so particle size of 2 mm with acid pretreatment at 2% reported the highest amount of TRS obtained with 42.03 g TRS / L solution.

Table 2. TRS for the process

Particle size (mm)	**Acid pretreatment conditions**	**TRS alkaline+acid pretreatment (g/L)**	**TRS hydrolysis (g/L)**	**Consolidated TRS - global process (g/L)**
0.5	2% H_2SO_4	11.125	27.833	38.958
	4% H_2SO_4	13.967	8.415	22.382
	6% H_2SO_4	9.094	11.447	20.541
1	2% H_2SO_4	12.458	26.524	38.982
	4% H_2SO_4	12.048	22.494	34.542
	6% H_2SO_4	7.641	22.706	30.257
2	2% H_2SO_4	10.697	31.333	42.030
	4% H_2SO_4	11.192	23.781	34.973
	6% H_2SO_4	9.886	20.272	30.158

These results showed that when combining alkaline, mechanic, and acid pretreatments, harsh conditions are not required for the acid treatment which avoids the formation of inhibitory compounds generated in the pretreatment stage.

Additionally, combined pretreatments require to include recovery stages of degraded sugars in the liquid fractions in order to make feasible the general application in the production process.

4. Conclusions

The pretreatment with H_2SO_4 at concentrations higher than 2% v/v has no significant effect on the process of sugar release after hydrolysis. The best conditions for a maximum conversion to TRS were achieved with a particle size of 2 mm and the combination of the pretreatments with NaOH and H_2SO_4 at 2% v/v, reporting 42.03 g glucose / L solution after global process. Minimum particle sizes and high acid concentrations are not the most favorable conditions in obtaining TRS by combining the studied pretreatments.
The corn stover is a hydrolysable lignocellulosic biomass with great potential due to its high cellulose content and low lignin content. However, new evaluations to less severe conditions must be carried out to define processes that are more environmentally-friendly. Additionally, the processes studied on a laboratory scale must be analyzed with the support of computational tools that allows the evaluation of industrial scale processes together with the environmental, economical, and energy profiles in order to generate recommendations for the integral use of these agro-industrial resources.

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