EVALUATION OF THE PRETREATMENT OF CORN STALK USING AN ULTRASOUND SYSTEM

Venturin, B.*[1]; Mulinari, J.[2]; Scapini, T.[3]; Camargo, A.F.[3]; Kunz, A.[4]; Treichel, H.[5]

[1]*PhD student in Agricultural Engineering – Western Paraná State University, Campus Cascavel, PR - Brazil,*
[2]*PhD student in Chemical Engineering - Federal University of Santa Catarina, Florianópolis, SC - Brazil,*
[3]*Mater's student in Environmental Science and Technology – Federal University of Fronteira Sul, Campus Erechim, RS – Brazil,*
[4]*Researcher at Embrapa Suínos e Aves, Concórdia, SC – Brazil,*
[5]*Professor at Federal University of Fronteira Sul, Campus Erechim, RS - Brazil.*

ABSTRACT: The growing demand for biofuels shows the need to significantly increase its production with high efficiency and in a sustainable way. This increase can be achieved with the full use of corn stalks and other biomasses. The lignocellulosic biomass has a high content of cellulose, which can be converted to different biocompounds. The great obstacle of this conversion is its complex chemical structure. So, the pretreatment of this material is a decisive step in the breakdown of its structure. This study evaluated the pretreatment through ultrasonic waves at the frequency of 40 kHz on corn stalk bran (*Zea mays*), using the experimental design methodology. The factors studied were liquid/solid ratio (3, 5, 7 g in 100 mL of H_2O), exposure time (22.5, 40, 57.5 min), temperature of the reaction medium (20, 50, 80 °C) and ultrasonic bath power (20, 50, 80% of 132 W). After being submitted to the pretreatment, the biomass was analyzed through high performance liquid chromatography. The concentrations of glucose, xylose, cellobiose, arabinose, acetic acid, furfural and hydroxymethylfurfural were determined in order to calculate the structural composition (cellulose, hemicellulose and lignin) of the material after the pretreatment. The statistical analysis of the experimental matrix showed that there were no significant changes in the composition of the pretreated biomass in the studied tracks. As the levels tested were very mild, the next step is to look for experimental conditions with higher irradiation energies of ultrasound waves, as well as higher exposure time and temperature of the reaction medium.

Keywords: biofuels, structural composition, chromatographic analysis.

INTRODUCTION

The issue of sustainable development has been widely discussed, with the highlight being the search for the expansion of the energy matrix. Thus, the need to replace the large-scale use of oil reserves by the use of biofuels is becoming increasingly clear. In this sense, lignocellulosic materials, which basically have cellulose, hemicellulose and lignin in their structure, are a promising alternative (Dagnino et al., 2013; Lizasoain et al., 2017).

This type of raw material has a high carbohydrate content, which are in polymer chains and can be saccharified and digested. The main obstacles to this conversion are to disassemble the resistant structure of the lignocellulosic biomass, effectively release the sugars susceptible to co-digestion and make its use economically viable (Paudel et al., 2017; Santos et al., 2012).

The pretreatment has a decisive role in the de-structuring of the complex chemical structures that forms the different lignocellulosic materials in order to facilitating the subsequent hydrolysis process, since after treated the material will present higher digestibility (Dinuccio et al., 2010; Zheng et al., 2014). The ideal pretreatment produces an easily digestible solid, does not degrade sugars, significantly removes lignin, does not inhibit the subsequent digestion step, produces waste without wasting the solid material, has a high degree of simplicity and is effective (Mosier et al., 2005; Pienkos and Zhang, 2009; Zhao et al., 2018).

In this context, the objective of this work was to investigate the pretreatment in an ultrasonic system of a lignocellulosic raw material, the corn stalk (*Zea mays*), using experimental design methodology.

MATERIAL AND METHODS

An amount of dry mass of crushed and sifted corn stalk (CSCS) was weighed into 250 mL erlenmeyers using an analytical balance (SHIMADZU AUY220, Philippines). The variables studied were dry mass (3, 5 and 7 g in 100 mL of H_2O), exposure time (22.5, 40 and 57.5 min), temperature of the reaction medium (20, 50 and 80 °C) and ultrasonic bath power (20, 50 and 80 % of 132 W). Considering the water from the intrinsic moisture of the CSCS, a final volume of 100 mL of H_2O was adjusted. The evaluated responses for this design were the structural composition of the crushed corn stalk after pretreatment in ultrasound system.

All experiments were carried out using the same volume of liquid (100 mL), therefore the interference of the liquid/solid ratio ($m.v^{-1}$) in the pretreatment performance could be evaluated. These 100 mL were placed in erlenmeyers containing the biomass, which were capped and taken to the ultrasonic bath (UNIQUE INC., USC-1800[a], operating frequency of 40 kHz and maximum power of 132 W - 0.42 $W.cm^{-2}$) (Nakashima et al., 2016; Nikolic et al., 2010). After the experiment time, the samples were removed from the ultrasound system, cooled to room temperature (25 °C) and filtered through a 100 μm nylon filter, the supernatant was discarded. The pretreated biomass was then washed with 1.5 L of distilled water until it reached pH 7.

The biomass retained in the nylon filter was dried until constant mass at 105 ºC in an oven (SOLAB SL-100, Brazil). After that, the samples were weighed in an analytical balance, stored in plastic bottles and frozen in a freezer at -4 ºC for later analysis of its structural composition according to the methodology described by Venturin et al. (2018).

RESULTS AND DISCUSSION

The composition of the sieved biomass after pretreatment in ultrasound system can be observed in Table 1. It can be observed that, practically, none of the experimental conditions tested changed the structural composition of the biomass. In results reported by Nakashima et al. (2016) and Nikolic et al. (2010), the ultrasound system proved to be effective to destabilize the lignocellulosic structure. However, different from this study, the authors used ultrasonic radiation with power up to 600 W and association with other solvents.

When all the results of cellulose, hemicellulose and lignin content were used, three mean values and their respective standard errors could be calculated, all of them in percentage ($m.m^{-1}$). They were 30.7 ± 0.4% for cellulose, 22.8 ± 0.3% for hemicellulose and 20.5 ± 0.4% for lignin. These values are very close to those obtained for the untreated CSCS, 29.7 ± 0.8% for cellulose, 23.3 ± 0.3% for hemicellulose and 21.8 ± 2.4% for lignin, which served as a parameter to verify the initial contents in the biomass composition.

By evaluating the effects of the variables for the three responses studied (cellulose, hemicellulose and lignin), it was observed that with 95% certainty none of the variables tested had a significant effect. Nakashima et al. (2016) studied the effect of isolated ultrasound in the biomass structure (stalk straw and corn leaves) and then analyzed the changes in the fiber through infrared spectroscopy using Fourier transform, with no change in composition. This result corroborates the ones presented in this paper.

The unsatisfactory results obtained can be attributed mainly to the very mild experimental conditions employed. Soft temperature values of the ultrasound system, associated with low ultrasound powers, were not able to disassemble the rigid lignocellulosic structure. The ultrasonic waves and the cavitation effect caused by them did not have a significant effect on the studied ranges. Probably by using higher ultrasonic powers, above 132 W (maximum provided by the equipment used for these tests), and other solvents, promising results can be obtained in the alteration of the lignocellulosic material composition (Mood et al., 2013; Sasmal and Mohanty, 2018). Ultrasound can be considered a clean energy, since no toxic chemicals are required and, when used in combination with solvents, it can reduce the amount of solvent needed in comparison to the conventional technique. These characteristics encourage the exploration of ultrasound for corn stalk pretreatment in order to use this biomass for the production of biofuels in future works.

CONCLUSIONS

Ultrasound pretreatment (UNIQUE INC., USC-1800[a], operating frequency of 40 kHz and maximum power of 132 W - 0.42 $W.cm^{-2}$) did not show significant changes in the structural composition of the corn stalk. So, its use in the experimental conditions studied is not recommended. However, it is expected that by using higher ultrasound power it will be possible to have significant effects on the lignocellulosic structure.

ACKNOWLEDGMENTS

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES) and by the Conselho Nacional de Desenvolvimento Científico e Tecnológico – Brazil (CNPq). The authors would like to thank CAPES and CNPq for the financial support.

REFERENCES

Dagnino, E.P., Chamorro, E.R., Romano, S.D., Felissia, F.E., Area, M.C., 2013. O*ptimization of the acid pretreatment of rice hulls to obtain fermentable sugars for bioethanol production*. Ind. Crops Prod. 42, 363–368

Dinuccio, E., Balsari, P., Gioelli, F., Menardo, S., 2010. *Evaluation of the biogas productivity potential of some italian agro-industrial biomasses*. Bioresour. Technol. 101, 3780–3783.

Lizasoain, J., Trulea, A., Gittinger, J., Kral, I., Piringer, G., Schedl, A., Nilsen, P.J., Potthast, A., Gronauer, A., Bauer, A., 2017. *Corn stover for biogas production: effect of steam explosion pretreatment on the gas yields and on the biodegradation kinetics of the primary structural compounds*. Bioresour. Technol. 244, 949–956.

Mood, S.H., Golfeshan, A.H., Tabatabei, M., Jouzani, G.S., Najafi, G.H., Gholami, M.,Ardjmand, M., 2013. *Lignocellulosic biomass to bioethanol, a comprehensiva review with a focua on pretreatment*. Renew. Sustain. Energy Rev. 27, 77–93.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M., 2005. *Features of promising technologies for pretreatment of lignocellulosic biomass*. Bioresour. Technol. 96, 673–686.

Nakashima, K., Ebi, Y., Kubo, M., Shibasaki-Kitakawa, N., Yonemoto, T., 2016. *Pretreatment combining ultrasound and sodium percarbonate under mild conditions for efficient degradation of corn stover*. Ultrason. Sonochem. 29, 455–460.

Nikolic, S., Mojovic, L., Rakin, M., Pejin, D., Pejin, J., 2010. *Ultrasound-assisted production of bioethanol by simultaneous saccharification and fermentation of corn meal*. Food Chem. 122, 216–222.

Paudel, S.R., Banjara, S.P., Choi, O.K., Park, K.Y., Kim, Y.M., Lee, J.W., 2017. *Pretreatment of agricultural biomass for anaerobic digestion: current state and challenges*. Bioresour. Technol. 245, 1194–1205.

Pienkos, P.T., Zhang, M., 2009. *Role of pretreatment and conditioning processes on toxicity of lignocellulosic biomass hydrolysates*. Cellulose 16, 743–762.

Santos, F. A, Queiróz, J.H. De, Colodette, J.L., Fernandes, S. A, Guimarães, V.M., 2012. *Potencial da palha de cana-de-aucar para produção de etanol*. Quim. Nova 35, 1004–1010.

Sasmal, S., Mohanty, K., 2018. *Pretreatment of lignocellulosic biomass toward biofuel production*. 203–221.

Venturin, B., Camargo, A.F., Scapini, T., Mulinari, J., Bonatto, C., Bazoti, S., Siqueira, D.P., Colla, L.M., Alves Jr, S.L., Bender, J.P., Steinmetz, R.L.R., Kunz, A., Fongaro, G., Treichel, H., 2018. *Effect of pretreatments on corn stalk chemical properties for biogas production purposes*. Bioresour. Technol. 266, 116-124.

Zhao, X., Luo, K., Zhang, Y., Zheng, Z., Cai, Y., Wen, B., Cui, Z., Wang, X., 2018. *Improving the methane yield of maize straw: focus on the effects of pretreatment with fungi and their secreted enzymes combined with sodium hydroxide*. Bioresour. Technol. 250, 204–213.

Zheng, Y., Zhao, J., Xu, F., Li, Y., 2014. *Pretreatment of lignocellulosic biomass for enhanced biogas production*. Prog. Energy Combust. Sci. 42.

Table 1. Structural composition of crushed and sieved corn stalk after pretreatment in ultrasound system, coded and real values.

Assay	Time (min)	Temperature (ºC)	Power (%)	Dry mass (g)	Cellulose (% $m.m^{-1}$)	Hemicellulose (% $m.m^{-1}$)	Lignin (% $m.m^{-1}$)
1	-1 (22.5)	-1 (42.5)	-1 (20)	-1 (3)	29.4	21.3	27.2
2	-1 (22.5)	-1 (42.5)	-1 (20)	1 (7)	30.2	22.4	17.8
3	-1 (22.5)	-1 (42.5)	1 (80)	-1 (3)	31.4	21	17.2
4	-1 (22.5)	-1 (42.5)	1 (80)	1 (7)	31.2	23.1	12.8
5	-1 (22.5)	1 (67.5)	-1 (20)	-1 (3)	31.3	23.5	19.4
6	-1 (22.5)	1 (67.5)	-1 (20)	1 (7)	29.7	22.2	22.5
7	-1 (22.5)	1 (67.5)	1 (80)	-1 (3)	32	23.4	18.8
8	-1 (22.5)	1 (67.5)	1 (80)	1 (7)	29.2	21.7	32
9	1 (57.5)	-1 (42.5)	-1 (20)	-1 (3)	30.7	22.9	17.6
10	1 (57.5)	-1 (42.5)	-1 (20)	1 (7)	31.3	23.3	21.3
11	1 (57.5)	-1 (42.5)	1 (80)	-1 (3)	31.1	23.5	20.7
12	1 (57.5)	-1 (42.5)	1 (80)	1 (7)	29.9	22.5	23.4
13	1 (57.5)	1 (67.5)	-1 (20)	-1 (3)	32.9	24.6	22.6
14	1 (57.5)	1 (67.5)	-1 (20)	1 (7)	33	24.7	25
15	1 (57.5)	1 (67.5)	1 (80)	-1 (3)	30.7	23	11.3
16	1 (57.5)	1 (67.5)	1 (80)	1 (7)	31.2	23.8	20.2
17 (C)	0 (40)	0 (55)	0 (50)	0 (5)	33.1	24.6	18.7
18 (C)	0 (40)	0 (55)	0 (50)	0 (5)	25	18.9	23
19 (C)	0 (40)	0 (55)	0 (50)	0 (5)	29.4	22.4	17.1