Optimization of the Soda-ethanol delignification in the biorefinery of rice husk

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Lignocellulosic materials are an interesting alternative to obtain products with high added value, such as bioethanol, food and cosmetics additives, and adhesives, among many others. Rice hulls (RHs) is an abundant residue in the Argentine Northeast region (provinces of Corrientes, Entre Rios, Santa Fe, Formosa and Chaco). Rice production in Argentina in 2012/13 reached 1,397,242 tons, of which about 20% was RHs [1]. RHs is composed of 48.7% carbohydrates (34.1% cellulose and 14.6% hemicelluloses), 17.2% and 1.8% of insoluble and soluble lignin acid respectively, 15% of inorganic components, and others [2], so the application of the biorefinery concept, i.e. the separation and valorization of its individual components, is of high interest. Delignification of RHs pretreated with acid (previously optimized process) [2] was carried out using an organosolv soda-ethanol process. This treatment is advantageous since the reaction is faster, it uses smaller amount of soda than the conventional soda process, and the ethanol can be recovered and reused. A Central Composite Experiment Design of two variables with three replicas of the center point was used. Soda concentrations between 9 and 17g per liter, and ethanol concentrations between 46 and 60% were evaluated. The liquor was placed in a reactor of AISI 316 stainless steel of 180ml, with a closing screw gauge. It was heated in a heat resistant silicone bath to 160°C. The reaction time was 60min, and it was necessary around additional 25min to reach 160°C. The mixture was then cooled in a cold water bath and filtered through a 100 mesh sieve. The solid was washed repeatedly to remove the remaining solution. The concentration of residual lignin (NREL process/TP-510-42618) in the pretreated solid was measured as response variable and delignification relative to initial lignin was calculated on this basis. The results were analyzed using multivariate analysis of variance (ANOVA). Statgraphics statistical software was used, with a level of significance of 95%. The adjusted model explained the 92% of the variability. Both variables showed significant effect ($p \le 0.05$) on the residual lignin in the treated solid. The percentage of delignification ranged from 63% in the treatment with 13g/l NaOH and 46% EtOH; to 87% in the treatment with 13g/l NaOH and 53% EtOH. The optimal response corresponded to 13g/l NaOH (center point) and 50% EtOH (-0.8 as coded variable), with a 3.26% theoreticalvalue of the residual lignin in the solid pretreated and an 87.9% of deslignification. In conclusion, the sequence acid / soda-ethanol allowed hemicelluloses extraction in the first stage and lignin extraction in the second stage. The residual solid was composed almost entirely of cellulose with approximately 25% of inorganic components, which will be separated in future studies, to fully implement the biorefinery concept.

References

[1] Planters Association of Corrientes of Rice and, Grain bag of Entre Rios.(2013) Specification, national rice Survey, Report campaign 2012/13: end harvest. http://www.acpaarrozcorrientes.org.ar/Informes arroceros/Informe.F...pdf [2] Dagnino, E. P., Chamorro, E. R., Romano, S. D., Felissia, F. E., Area, M. C. (2013). Optimization of the acid pretreatment step of rice hulls for bioethanol production. *Industrial Crops and Products* 42, 363-368.