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# Optimization and kinetics study of solvent pretreatment of South African corn cob for succinic acid production

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**2018**

https://hdl.handle.net/10539/24033

Mudzanani, Khuthadzo Edna (2018) Optimization and kinetics study of solvent pretreatment of South African corn cob for succinic acid production, University of the Witwatersrand, <https://hdl.handle.net/10539/24033>

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# ABSTRACT

Increasing concerns over environmental and geo-political issues on resources' sustainability have driven the industries to shift their efforts to produce chemicals from renewable biomass. Amongst the lignocellulosic biomass, corncob contains cellulose, hemicellulose and lignin that are built in a compact structure which makes it difficult to access. Pre-treatment is then applied to make the content to be accessible to enzymatic hydrolysis which breaks down the polysaccharides to monomers. The sugar monomers can be converted to a wide range of bio-products such as biofuels and bio-chemicals. The objective of the study was to determine, evaluate and optimize the best solvent system to pre-treat corn cob. In addition, the study evaluated the effect of pre-treatment parameters on the yield of cellulose and hemicellulose and attempt to develop a kinetic model to explain the dissolution.

Lithium perchlorate, zinc chloride, phosphoric acid, sulphuric acid and sodium hydroxide were used during the pre-treatment, which was carried out at 70-80 ° C for 6 hours. Characterization of pre-treated samples showed a significant change in structure after pre-treatment indicating disruption in cell wall of the lignocellulosic material. FTIR revealed a reduction in phenolic group; indicating that the lignin content has been reduced. The XRD patterns show that crystallinity was considerably reduced; this was shown by an increase in calculated crystallinity index (CrI) after $LiClO_4$, $ZnCl_2$, $H_3PO_4$ and NaOH pre-treatment. The CrI of raw corncob (CrI= 32.7%) increased to 46.2 %, 42.3 %, 55.6 % and 53.4 % of $LiClO_4$, $ZnCl_2$, $H_3PO_4$ and NaOH, respectively. The crystallinity index increased for pre-treated material, indicating that the amorphous cellulose is dissolved in the liquor, as well as lignin and hemicellulose removal

This study has shown that $LiClO_4.2H_2O$ pretreatment agent is an efficient solvent system to pretreat corncob which consecutively increase the accessibility of cellulose and hemicellulose from the solid fractions. The accessibility was confirmed by an ease hydrolysis of cellulose & hemicellulose to glucose & xylose respectively. An increase of nearly four times compared to the untreated corncob. The effect of reaction operating parameters i.e. Reaction time, temperature and solvent concentration was carried out and then optimized by response surface methodology (RSM) using Minitab 16. The target was to maximize the yield of cellulose and hemicellulose. It was discovered that the increase in temperature and reaction time increase the accessibility of cellulose and hemicellulose until an equilibrium is reached at 3 & half hours and 176 °c. The pretreatment solvent concentration was discovered to have an effect on the accessibility but not as much as temperature and time. The best pretreatment

conditions to obtain high polysaccharides conversions to monomers were at 176°c for 3.5 hours using $LiClO_4.2H_2O$ for 10 g of corncob.

The results obtained from RSM were used to evaluate the temperatures profile, kinetic model for the corncob pretreatment as a function of temperature. The kinetics of pretreatment were studied by the amount of glucose, xylose and the lignin removed from the pretreated solids. The kinetic model of lignin removal and sugars accessibility was identified as a first-order reaction corresponding to the bulk phase for pretreatment time up to 24 hours. The rate constant results show that the kinetic rate increased with temperature. The activation energy for glucose, xylose and lignin were calculated to be 15.0 kJ/mol, 14.2 kJ/mol and 36.54 kJ/mol, respectively.