# A Co-production of Sugars, Lignosulphonate, Cellulose and Cellulose Nano-crystals from Ball-milled Wood

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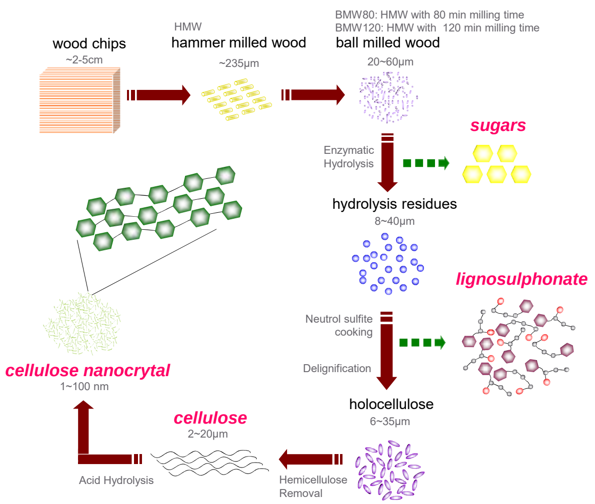
## Introduction

Lignocellulose biomass can be converted to high-value products by separation and transformation of its three components. However, various reported methods usually use one of components, getting rid of the others. They can not utilize the all components (cellulose, hemicellulose and lignin) with low cost and high efficiency. Valorization of all components have become clearly important in developing cost-effective biorefineries. Ball milling acted as a physical pretreatment reduces the wood particle size and crystallinity, and facilitates the fractionation and saccharification. It also shortens the hydrolysis time for harvesting the nanocellulose. It is deemed as a potential pretreatment for the production of cellulosic sugars. The saccharification residual solids from hydrolyzing the milled wood contains the most recalcitrant cellulose and high percentage of lignin. Harvesting these components for cellulose and value - added lignin products will bring additional revenues to help a sustainable bioconversion.

## Objectives

- Demonstrate the feasibility of utilizing major components of ball milled wood and hydrolysis residual solids,
- Evaluate the effects of ball milling on 4 co-products: sugars, lignosulpohonate, cellulose and cellulose nanocrystal, and the role in facilitating preparations of alpha cellulose and cellulose nanocrystals.

## Materials and Method




## Results

## Sugar Yields and Lignosulphonate Content

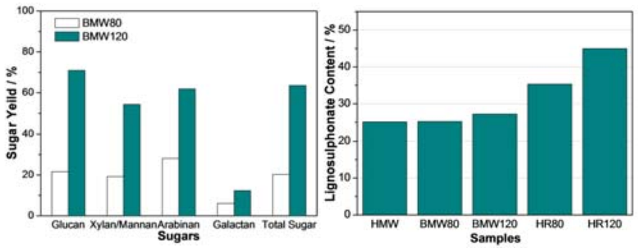



Fig. 1 Sugar yeilds, and lignosulphonate content of ball milled wood

## Morphology

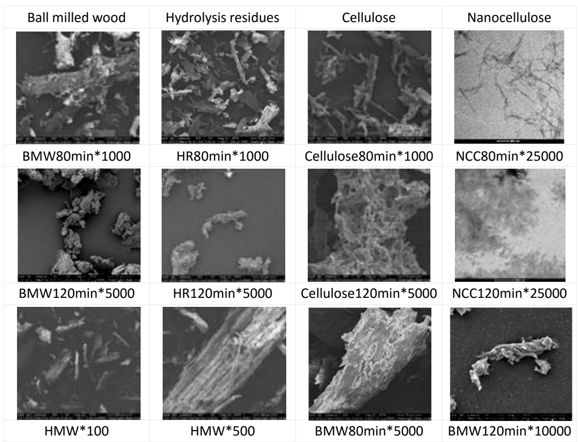



Fig. 2 Morphology of hammer milled wood, ball milled wood, hydrolysis residues, and cellulose

## Aspect Ratio

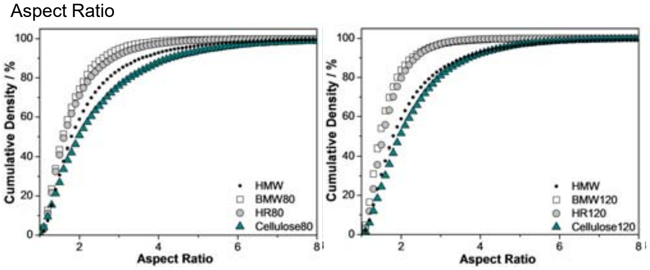



Fig. 3 Cumulative aspect ratio distribution of the ball milled wood, hydrolysis residues and cellulose

## Crystallinity

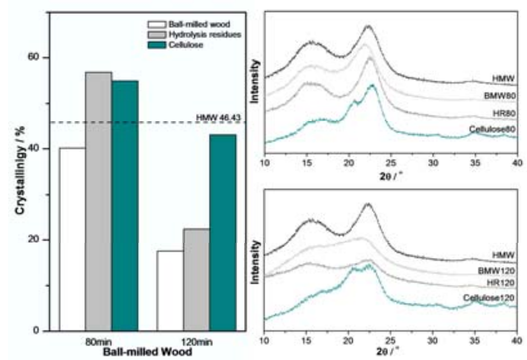



Fig. 4 X-ray powder diffractograms (right) and crystallinity index based on Segal method of the ball-milled wood, Hydrolysis residues, and resulted cellulose

## Conclusions

- Lingosulphonate, cellulose, and cellulose nanocrystal are successfully prepeared by using ball milled wood and enzymatic hydrolysis residues.
- Sufficient ball mill not only improve the sugar yield, but also shortens the hydrolysis time for nanocellulose, only 15-30 min.
- BMWs present an intuitive view of particle size reduction with prolonging milling time. Ball milling decreases the aspect ratio of wood fibers, while the lignin, hemicelluose removal shapes the cellulose, increasing its aspect ratio gradually.
- Ball milling hardly affects the resulted lignosulphonate content. Enzymatic hydrolysis has a great contribution to fractionation of lignin.
- Ball mill process damages the well organized fiber structure, reducing their crystallinigy. However, enzymatic hydrolysis increase the crystallinity of remaining cellulose by removing the amorphous cellulose. Hemicellulose removal process transform a portion of Cellulose I to Cellulose II.

## Acknowledgments

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References:

[1] Chattopadhyay, P. P, Manna, I., Talapatra, S., et al., 2001. A mathematical analysis of milling mechanics in a planetary ball mill. Materials Chemistry and Physics, 68(1), 85-94.

[2] Avolio, R., Bonadies, I., Capitani, D., Errico, M.E., Gentile, G., Avella, M., 2012. A multitechnique approach to assess the effect of ball milling on cellulose. Carbohydrate Polymers, 87, 265-273.

[3] Zhang, W., Liang, M., Lu, C., 2007. Morphological and structural development of hardwood cellulose during mechanochemical pretreatment in solid state through pan-milling. Cellulose, 14, 447-456.

[4] Zhu, J.Y., Sabo, R., Luo, X., 2011. Integrated production of nano-fibrillated cellulose and cellulosic biofuel (ethanol) by enzymatic fractionation of wood fibers. Green Chemistry, 13, 1339-1344.

[5] Millett, M. A., Effland, M. J., and Caulfield, D. F. 1979. Influence of Fine Grinding on Hydrolysis of Cellulosic Materials-Acid Vs. Enzymatic[J]. Advances in Chemistry Series, 181, 71-89.

[6] Guerra, A., Filpponen, I., Lucia, L.A., Saquing, C., Baumberger, S., Argyropoulos, D.S., 2006. Toward a Better Understanding of the Lignin Isolation Process from Wood. Journal Of Agricultural And Food Chemistry, 54, 5939-5947.

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