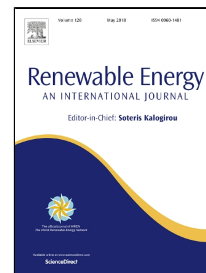


# Accepted Manuscript

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PII: S0960-1481(18)30223-4  
DOI: 10.1016/j.renene.2018.02.079  
Reference: RENE 9810  
To appear in: *Renewable Energy*  
Received Date: 23 April 2017  
Revised Date: 29 January 2018  
Accepted Date: 17 February 2018

Please cite this article as: Xiang Li, Mi Li, Yunqiao Pu, Arthur J. Ragauskas, Adam S. Klett, Mark Thies, Yi Zheng, Inhibitory Effects of Lignin on Enzymatic Hydrolysis: The Role of Lignin Chemistry and Molecular Weight, *Renewable Energy* (2018), doi: 10.1016/j.renene.2018.02.079

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# Inhibitory Effects of Lignin on Enzymatic Hydrolysis: The Role of Lignin Chemistry and Molecular Weight

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## Abstract:

Lignocellulose is a promising feedstock for biofuel production, while lignin poses a grand challenge on the entire process, especially enzymatic hydrolysis. In this study, different types of lignin inhibited enzymatic hydrolysis by different mechanisms. Organosolv lignin from Loblolly pine adsorbed enzyme nonproductively and reduced the available enzyme for cellulose, therefore decreasing hydrolysis rate and ultimate sugar yield. Kraft pine lignin precipitated on the surface of cellulose, preventing it from contacting with enzyme. The molecular weight influenced the inhibition effect of lignin. Lignin of lower molecular weight could bind enzyme nonproductively and when the molecular weight increased, the steric repulsion caused by lignin deposition on cellulose became more significant. The NMR analysis revealed that lignin structural features, e.g., functional groups, S/G ratio, determined the behaviors of lignin in enzymatic hydrolysis. High content of aliphatic hydroxyl groups, or low content of carboxylic groups led to high surface hydrophobicity, increasing the adsorption between lignin and enzyme. In addition, the substrate reactivity is also an important factor that affects enzymatic hydrolysis. Cellulose with higher crystallinity exhibited slower hydrolysis rate and lower conversion. When the crystallinity index increased from 0.43 to 0.72 and 0.81, the ultimate conversion decreased from 80 to 68% and 57%, respectively.

**Keywords:** Lignocellulose; enzymatic hydrolysis; nonproductive adsorption; lignin chemistry; molecular weight

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