MULTISCALE DYNAMICS OF HEMICELLULOSE HYDROLYSIS FOR BIOFUEL PRODUCTION

Sajal Kanti Dutta and Saikat Chakraborty[*]
Department of Chemical Engineering, Indian Institute of Technology Kharagpur
Kharagpur 721302, India

Abstract

This work uses a tightly-coupled experimental and modelling approach to show that the enzymatic hydrolysis of hemicellulose for biofuel production is a multiscale process, in which the pore scale plays a determining role in enzyme adsorption and solid phase hydrolysis. At the molecular scale, the products (xylose and xylobiose) inhibit the hydrolysis non-competitively, and the nature of product inhibition remains unaltered by reactor mixing. We develop an 'optimal mixing' strategy that enhances soluble sugar yield by up to 20% while saving energy, and illustrate how spatial patterns in tubular reactors further increase sugar yields by 6% over 'optimal mixing'.

[*] To whom all correspondence should be addressed

Introduction

Hemicelluloses are the earth's second most abundant structural polymers, found in lignocellulosic biomass. Efficient enzymatic depolymerization of hemicelluloses by cleaving their β-(1→4)-glycosidic bonds to produce soluble sugars is instrumental to the cost-effective production of liquid biofuels (Dutta and Chakraborty, 2015). Here we use a tightly-coupled experimental and theoretical analysis to show that the enzymatic hydrolysis of hemicellulose is a multiscale reactive process comprising of molecular scale, pore scale, and reactor scale, and that the complex, coupled interactions between the scales, leading to oscillatory spatial patterns in the reactor, improve sugar yields.

Results and Discussion

Our substrate characterization results show that the average pore size of xylan is 9.8 nm, which is tenfold smaller than its average molecular size (109 nm), which in turn is significantly smaller than the reactor length scale. Thus, the pore scale is the smallest of the three scales involved in hemicellulose hydrolysis, and therefore, the sequence of length of scales is: *Reactor scale > Molecular scale > Pore scale* (Dutta and Chakraborty, 2016), which is a deviation from the classical sequence of scales in most multiscale reactive processes.

Adsorption of enzymes to solid xylan particles is the first step in hemicellulose hydrolysis, followed by the enzymatic cleaving of β-(1→4)-glycosidic bonds in the solid and liquid phases. Our experiments show that enzyme adsorption occurs primarily on the pore surface, and that the adsorption, which is initially non-equilibrium, attains equilibrium at 5 h. Our particle size analysis shows that the hydrolysis system, which is dominated by the surface reaction/ molecular scale in the first 10 min manifested by 45-54% decrease in particle size, is driven by two to fourfold swelling and reaction at the pore scale, leading its porosity to increase to 84-96% in the first 5 h. Further analyses performed by blocking the pores of the xylan particles show that more than 75% of the total soluble sugars produced are from pore scale hydrolysis. Timescale analysis of the transport and reaction processes show that pore scale reactive dissolution and particle swelling determine the overall time required to produce soluble sugar from solid hemicellulose.

Our experimental results show that the hemicellulose hydrolyses in both liquid and solid phases are found to be non-competitively inhibited at the molecular scale by the products xylose and xylobiose, with the inhibition being more potent in the liquid phase. The optimum solid loading is obtained as 5 mg/ml, above which substrate inhibition sets in. Our model-experiment comparisons allow us to quantify the adsorption and desorption rate constants and the xylobiose inhibition constants in the solid and liquid phases.

Our reactor scale analysis shows that reactor mixing does not alter the non-competitive nature of product inhibition, but produces stronger inhibition that results in 8-15% reduction of sugar yield, as the mixing speed increases from 0 to 200 rpm. The kinetic constants (K_m, V_{max}, K_x) assume mass-transfer disguised values at no or low mixing speed. An optimal mixing strategy, comprising of 55-70 min of initial rapid macromixing followed by micromixing for the rest of the hydrolysis, increases xylose and reducing sugar yields by 6.3-8% and 13-20%, respectively, over continuous mixing at 200 rpm, for 1-5 mg/ml substrate loading at an optimum enzyme to substrate ratio of 1:20, with an energy saving of 94-96% over 24 h (Dutta and Chakraborty, 2018).

We also show that the interaction between activator-inhibitor type molecular reaction and micromixing leads to oscillatory spatial patterns in tubular reactors, which increase reducing sugar yields by 9-11%, 16-19%, and 3-6% over no mixing (0 rpm), continuous mixing (150 rpm), and optimal mixing, respectively, while xylose yield increases by 4-5%, 7-9%, and 2.8-3.2%, respectively, for 1-5 mg/ml substrate loading. Thus, we illustrate how the complex, coupled interactions between the three scales can be used to engineer an enhancement of soluble sugar and bioethanol yields.

Conclusions

We use a tightly-coupled experimental and modelling approach to show that the enzymatic hydrolysis of hemicellulose for biofuel production is a multiscale process, in which the pore scale plays a determining role in enzyme adsorption and solid phase hydrolysis. At the molecular scale, the products (xylose and xylobiose) inhibit the hydrolysis non-competitively, and the nature of product inhibition remains unaltered by reactor mixing. We develop an 'optimal mixing' strategy that enhances soluble sugar yield by up to 20%, while saving energy. We illustrate how spatial patterns in tubular reactors further increase sugar yields by 6% over 'optimal mixing'.

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