Implication of Fractal Kinetics and Diffusion Limited Reaction on Biomass Hydrolysis

Authors : Sibashish Baksi, Ujjaini Sarkar, Sudeshna Saha

Abstract : In the present study, hydrolysis of Pinus roxburghi wood powder was carried out with Viscozyme, and kinetics of the hydrolysis has been investigated. Finely ground sawdust is submerged into 2% agueous peroxide solution (pH=11.5) and pretreated through autoclaving, probe sonication, and alkaline peroxide pretreatment. Afterward, the pretreated material is subjected to hydrolysis. A chain of experiments was executed with delignified biomass (50 g/l) and varying enzyme concentrations (24.2-60.5 g/l). In the present study, 14.32 g/l of glucose, along with 7.35 g/l of xylose, have been recovered with a viscozyme concentration of 48.8 g/l and the same condition was treated as optimum condition. Additionally, thermal deactivation of viscozyme has been investigated and found to be gradually decreasing with escalated enzyme loading from 48.4 g/l (dissociation constant= 0.05 h⁻¹) to 60.5 g/l (dissociation constant= 0.02 h⁻¹). The hydrolysis reaction is a pseudo first-order reaction, and therefore, the rate of the hydrolysis can be expressed as a fractal-like kinetic equation that communicates between the product concentration and hydrolytic time t. It is seen that the value of rate constant (K) increases from 0.008 to 0.017 with augmented enzyme concentration from 24.2 g/l to 60.5 g/l. Greater value of K is associated with stronger enzyme binding capacity of the substrate mass. However, escalated concentration of supplied enzyme ensures improved interaction with more substrate molecules resulting in an enhanced de-polymerization of the polymeric sugar chains per unit time which eventually modifies the physiochemical structure of biomass. All fractal dimensions are in between 0 and 1. Lower the value of fractal dimension, more easily the biomass get hydrolyzed. It can be seen that with increased enzyme concentration from 24.2 g/l to 48.4 g/l, the values of fractal dimension go down from 0.1 to 0.044. This indicates that the presence of more enzyme molecules can more easily hydrolyze the substrate. However, an increased value has been observed with a further increment of enzyme concentration to 60.5g/l because of diffusional limitation. It is evident that the hydrolysis reaction system is a heterogeneous organization, and the product formation rate depends strongly on the enzyme diffusion resistances caused by the rate-limiting structures of the substrate-enzyme complex. Value of the rate constant increases from 1.061 to 2.610 with escalated enzyme concentration from 24.2 to 48.4 g/l. As the rate constant is proportional to Fick's diffusion coefficient, it can be assumed that with a higher concentration of enzyme, a larger amount of enzyme mass dM diffuses into the substrate through the surface dF per unit time dt. Therefore, a higher rate constant value is associated with a faster diffusion of enzyme into the substrate. Regression analysis of time curves with various enzyme concentrations shows that diffusion resistant constant increases from 0.3 to 0.51 for the first two enzyme concentrations and again decreases with enzyme concentration of 60.5 g/l. During diffusion in a differential scale, the enzyme also experiences a greater resistance during diffusion of larger dM through dF in dt.

Keywords : viscozyme, glucose, fractal kinetics, thermal deactivation

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