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Optimization of enzyme loading and hydrolytic time in the hydrolysis of mixtures of cotton gin waste and recycled paper sludge for the maximum profit rate

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ABSTRACT

The hydrolytic kinetics of mixtures of cotton gin waste (CGW) and recycled paper sludge (RPS) at various initial enzyme concentrations of Spezyme™ AO3117 was investigated. The experiments showed that the concentrations of reducing sugars and the conversions of the mixtures increased with increasing initial enzyme concentration. The reducing sugar concentration and conversion of the mixture of 75% CGW and 25% RPS were higher than those of the mixture of 80% CGW and 20% RPS. The conversion of the former can reach 73.8% after a 72-h hydrolysis at the initial enzyme loading of 17.4 Filter Paper Unit (FPU)/g substrate. A three-parameter kinetic model based on enzyme deactivation and its analytical expression were derived. Using nonlinear regression, the parameters of the model were determined for the experimental data of hydrolytic kinetics of the mixtures. Based on this kinetic model of hydrolysis, two profit rate models, representing two kinds of operating modes with and without feedstock recycling, were developed. Using the profit rate models, the optimal enzyme loading and hydrolytic time can be predicted for the maximum profit rate in ethanol production according to the costs of enzyme and operation, enzyme loading, and ethanol market price. Simulated results from the models based on the experimental data of hydrolysis of the mixture of 75% CGW and 25% RPS showed that use of a high substrate concentration and an operating mode with feedstock recycle can greatly increase the profit rate in ethanol production. The results also demonstrated that the hydrolysis at a low enzyme loading is economically required for systematic optimization of ethanol production.

1. Introduction

Cotton gin waste (CGW) and recycled paper sludge (RPS) are two residues from the cotton and paper manufacturing industries. It was estimated that about 2.04 million tons of CGW and 4 million dry tons of RPS were generated annually by the U.S. cotton and papermaking industries, respectively [1,2]. The traditional disposal methods, including landfilling, land application, and incineration [3], of the two wastes have some disadvantages, such as environmental pollution and limitation of land supply etc. Both CGW and RPS contain about 50% or more cellulose and hemicellulosic components [4,5] that can be used to produce bio-ethanol. The conversion of CGW and RPS to bio-ethanol has been investigated by some researchers [4–10]. However, there is no publication on the hydrolysis and ethanol production from the mixture of CGW and RPS.

On the other hand, the optimization of process parameters, including hydrolytic temperature, pH, time, and enzyme loading, has been of interest to researchers for enhancing the process competitiveness. The optimal hydrolytic temperature and pH can be obtained through experimental investigation of the maximum sugar concentration at various ranges of temperature and pH or through a combination of experiment and modeling. However, determining an optimal enzyme loading and hydrolytic time is still a challenge for researchers, because sugar concentrations in the hydrolysate often increase monotonically with increasing enzyme loading and hydrolytic time. Thus, the sugar concentration cannot be an objective function for the optimization of enzyme loading and hydrolytic time. Rather, the objective function can be profit or profit rate produced by the hydrolytic process. de Halleux et al. [11] developed a simple cost model to calculate the optimal hydrolytic time for ethanol production from lignocellulosic biomass. However, there is no published model that can be used for optimal enzyme loading. Another barrier to commercial production of bio-ethanol from lingocellulosic materials is the high cost of enzyme, which necessitates the use of low enzyme loading. However, low enzyme loading often results in a higher conversion cost due to a low lignocellulosic conversion during hydrolysis. An alternative method to compensate for a low conversion is adopting a recycle process in which the remaining lignocellulosic materials are

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Nomenclature

a	constant in Eq. (19) (l/g)
b	constant in Eq. (19) (-)
B	constant in Eq. (15) (-)
c_b	feedstock cost based on gram substrate ($/g substrate)
c'_b	feedstock cost based on liter ethanol ($/l ethanol)
c_E	enzyme cost ($/g enzyme)
c_g	sugar market price in unit sugar weight ($/g sugars)
c_h	hydrolysis cost on gram substrate ($/g substrate)
c'_h	hydrolysis cost based on liter ethanol ($/l ethanol)
c_o	operation cost on gram substrate ($/g substrate)
c'_o	operation cost based on liter ethanol ($/l ethanol)
C_c	carbohydrate concentration in Eq. (34) (g/l)
C_s	reducing sugar concentration of the filtrate in Eq. (34) (g/l)
E	enzyme concentration (g/l)
E_0	initial enzyme concentration (g/l)
E_d	enzyme loading based on the dried substrate (FPU/g)
f	sugar production cost in unit reactor volume ($/l hydrolytic volume)
k_1	rate constant of forward reaction in Eq. (1) (l/(g h))
k_{-1}	rate constant of backward reaction in Eq. (1) (/h)
k_2	enzyme deactivation rate constant (l/(g h))
$k_{2,ave}$	average value of k_2 in Eq. (21) (l/(g h))
k_3	rate constant of the product formation (/h)
K_e	equilibrium constant in Eq. (8) (g/l)
$K_{e,ave}$	average value of K_e in Eq. (21) (g/l)
m	total number of initial enzyme concentration
m_b	sample weight of the autoclaved suspension in ASTM E1721-95 procedure (g)
m_c	carbohydrate contents of mixtures in mass percentage (%)
n	total number of experimental points for an initial enzyme concentrations
P	product (sugar) concentration (g/l)
p_f	ratio of profit rate to production cost for cycle (/h)
p_{fn}	ratio of profit rate to production cost for non-cycle (/h)
p_r	profit in unit reactor volume ($/l hydrolytic volume)
p'_r	profit rate with feedback recycle ($/l hydrolytic volume and time)
p'_{rn}	profit rate without feedback recycle ($/l hydrolytic volume and time)
p_s	sugar market price ($/l hydrolytic volume)
r	constant of average conversion factor from cellulose and hemicellulose to sugars
R_0	reaction ordinate (dimensionless)
R_1	conversion factor from substrate to ethanol) (l ethanol/g substrate)
R_2	conversion factor from cellulose to substrate (g substrate/g cellulose)
R_3	fraction of sugar market price in ethanol market price
S	convertible carbohydrate in insoluble substrate based on conversion of cellulose to glucose (g/l)
S_0	initial substrate concentration (g/l)
SE^*	effective complex concentration (g/l)
SE^*_{in}	ineffective complex concentration (g/l)
t	residence time (h)
t_s	residence time in steam explosion (min)
T_b	base temperature in Eq. (31) (°C)
T_r	explosion temperature in Eq. (31) (°C)
v_f	final volume of the filtrate after pH adjustment (l)
v_i	initial volume of the filtrate before pH adjustment (l)
w	weight factor in Eq. (20) determined by variance
x	conversion (dimensionless)
x_c	predicted conversion (dimensionless)

Subscripts

i	index number of initial enzyme concentration
j	index number of the experimental points
op	optimal condition

recycled for hydrolysis, but this operation may increase the operating cost. Hence, a quantitative study on the benefits between the low enzyme loading and the recycle process with a higher operating cost is required to maximize the profit rate for ethanol production.

Several economic evaluations of bio-ethanol production from lignocellulose materials using enzyme hydrolysis have been reported in published literature [12]. However, the results from these studies did not provide guidance on the adjustments of enzyme dosage and hydrolytic time when the hydrolytic and market factors change to maximize profit in ethanol production. For such an objective, a mathematical model combined with hydrolytic and profit factors is required, which is different in the Helleux et al.'s model that is based on production cost with hydrolytic time as an objective function [11]. The first step in this combined model is to establish a kinetic model of the enzymatic hydrolysis. The proposed empirical and mechanistic models of enzymatic hydrolysis in literature cannot be applied to such an objective model because of limitations such as un-convergent characteristic for substrate conversion, no analytical solution, and too many parameters etc. [13–16]. Therefore, it is necessary to develop a novel model with the following characteristics: a model with an analytical solution, a good convergence for substrate conversion, few parameters, and easy parametric determination. The second step in this combined model is to develop a profit rate model that relates the profit rate with various factors influencing hydrolysis such as operating cost, enzyme cost, and substrate conversion etc. Using such a profit rate model, the enzyme loading and hydrolytic time can be adjusted to obtain the maximum profit rate according to the changes in operating and market factors.

The objectives of this study were: (1) to investigate enzymatic hydrolytic kinetics of various mixtures of CGW and RPS, and to optimize the ratio of the mixtures; (2) to develop a novel model of enzymatic hydrolysis with convergent property as a basis for profit rate models; (3) to determine the values of the kinetic model parameters for the mixtures of CGW and RPS; (4) to develop profit rate models which included both the influencing hydrolytic and profit factors, and to optimize enzyme loading and hydrolytic time for maximum profit rates.

2. Model development

2.1. Enzymatic hydrolysis model

Assumptions of the model:

(1) The endo-β-1,4-glucanase, exo-β-1,4-cellobiohydrolase, and glycosidase enzymes were assumed to form a single combined