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Research paper

Optimal control of enzymatic hydrolysis of lignocellulosic biomass

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Abstract

Cellulose hydrolysis is a key step in lignocellulosic ethanol production. At present, commercial production of lignocellulosic ethanol is limited due to the long hydrolysis times and requirement of large quantity of expensive enzymes. Therefore, reduction of the enzyme consumption as well as hydrolysis time is crucial and model based optimisation methods can be used for the same. A semi-mechanistic model with cellobiose, glucose, and xylose inhibition with Arrhenius based relationship between temperature and kinetic parameters and thermal deactivation of enzymes was used for the present study. Optimal control problem with temperature as control variable was formulated after considering two different objective functions. For the objective of glucose concentration maximisation at final batch time, the benefit of implementing optimal control increased with reducing batch times. For the batch time of 24 hours, the final glucose concentration increased by 3.2%. For the objective of batch time minimisation, the reduction of batch time was 5.8% and it was observed for a target glucose concentration of 45 g/kg of cellulose. The use of optimal control can reduce the enzyme requirement up to 77.8% of endoglucanase and exoglucanase for glucose maximisation and 22.2% for batch time minimisation. The above results show the usefulness of optimal temperature control in increasing the glucose concentration, and reducing the batch time without increasing the enzyme used.

Keywords: Enzymatic hydrolysis; Optimal control; Temperature; Batch time; Glucose concentration

1. Introduction

In lignocellulosic ethanol production, the hydrolysis of lignocellulose is important because it decides the amount of glucose that is offered for fermentation [1]. The polymeric sugars like cellulose and hemicellulose are converted to their corresponding monomers by chemical, physicochemical and biological methods. Chemical methods utilise either an acid or an alkali whereas, physico-chemical methods utilise high temperature, high pressure along with a chemical reagent [2]. These methods are energy intensive and are prone to produce degradation products which are not desirable. Therefore, partial degradation of cellulose, hemicellulose and lignin is done by the chemical or physicochemical methods which expose the cellulosic substrate for further hydrolysis under mild conditions by using enzymes like cellulase [3].

The enzymatic hydrolysis of cellulose is the result of synergistic action of multiple enzyme components having different mechanisms of action. These enzymes are found commonly in fungal species like *Penicillium verruculosum, Trichoderma reesei, Aspergillus niger, Sporotrichum Thermophile* [4–7]. Hydrolytic enzymes are also available as commercial preparations like Celluclast, Cellic CTec2, Speczyme CP, Novozyme 188, Cytolase CL, and Accellerase [8–12]. The components of cellulase are endoglucanases, exoglucanases and β-glucosidases. The fraction of each of these components in a given enzyme mixture is dependent on the source of the enzyme. The endoglucanases bind to the cellulose and exposes the reducing and non-reducing ends resulting in the formation of cellooligomers. The exoglucanases bind to the reducing and non-reducing ends of the cellooligomers converting the same to cellobiose. The final component that acts is the β-glucosidase which converts cellobiose to glucose [13]. The insufficient quantity of β-glucosidases in the enzyme mixture leads to accumulation of cellobiose which inhibits the hydrolysis reactions. Apart from cellobiose, the glucose, cellooligomers, and xylose also inhibit the hydrolysis reaction. Lignin reduces the enzyme available for hydrolysis by non-productive adsorption. In addition to the quantity of enzyme, maintaining optimal operating conditions like temperature and pH is also important. The typical operating temperature for cellulose hydrolysis ranges between 40 and 55 °C and pH

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Table 1
Solutions proposed and their drawbacks in cellulose hydrolysis process.

S. no.	Challenges	Solutions	Drawbacks
1.	Cellobiose accumulation and inhibition	1. Additional supplementation of β-glucosidase in hydrolysis 2. Engineered yeast that can produce β-glucosidase for SSF [9]	Increase in the total cost due to additional supplementation
2.	Glucose inhibition	1. Simultaneous Saccharification and Fermentation (SSF) 2. Glucose tolerant enzymes [16]	In case of SSF, • Ethanol inhibition • Difference in optimum temperature for hydrolysis and fermentation [17]
3.	Lignin adsorption	Adding proteins or surfactants [18]	Cost of additional protein/surfactant
4.	Degradation products form pretreatment	1. Detoxification [19] 2. Less calcitrant feedstock and mild conditions for pretreatment [19]	1. Cost associated with additional processing step [19] 2. Poor sugar yield in pretreatment [19]
5.	Low solid loading	Continuous feeding of substrate and/or enzyme in a fed-batch reactor	With increase in the substrate content, the amount of glucose inhibition is also higher
6.	Enzyme cost	1. Recycling the enzymes by readsorption 2. Using engineered enzymes with higher efficiency [20] 3. Improving the efficiency of the process by optimisation [21].	Recycling by readsorption is not suitable for β-glucosidase

ranges from 4.5 to 5.5. The enzymes are susceptible to degradation upon exposure to high temperature, and mixing speed [14,15]. The condition in which the enzyme starts degrading is dependent on the source of enzyme.

Different strategies were proposed in the literature to overcome the challenges in enzymatic hydrolysis of lignocellulose. Table 1 list some of these strategies along with their drawbacks. The solutions suggested in Table 1 recommend modifying either the enzyme source or the process to overcome the above mentioned challenges.

While improvements in enzymes and process development are expensive and long term solutions, optimising the process operations to improve economic feasibility can develop a short term solution. Moreover, process optimisation is anyway essential for commercial operation of the plant. Considering the complexity and nonlinearity of the process, model based optimisation using systematic models is more appropriate than through heuristic strategies. The focus of this work is to increase the glucose yield and reduce the batch time by using optimal temperature control. Previously, studies on dynamic optimisation by controlling feeding strategies of substrate, and enzyme for fed-batch reactor were done. These studies have demonstrated the increase in solid loading up to 20% in fed-batch reactor [22]. Owing to the higher chances of contamination at longer batch times, and inhibition by accumulated glucose in fed-batch reactors, the present study is done for batch reactor. Among the parameters for batch hydrolysis of cellulose, since temperature is more sensitive as well as controllable, temperature is chosen as the control variable for the present study [23].

The paper is organised as follows. The process of enzymatic hydrolysis of cellulose is explained in section 2. The kinetic modelling of cellulose hydrolysis is presented in section 3. Section 4 explains the optimal control problem formulation. The results of maximisation of glucose concentration and minimisation of hydrolysis time studies are explained in section 5. Section 6 concludes the paper.

2. Enzymatic hydrolysis process

Lignocellulosic biomass is generally pretreated where the objective is to disrupt the cellular matrix to make the cellulose accessible to enzymes. The pretreated biomass is then sent for enzymatic hydrolysis. The enzymatic hydrolysis of cellulose is a heterogeneous reaction; therefore, the first step in cellulose hydrolysis is the binding of the enzymes to the substrate by adsorption. The bound fraction of endoglucanase and exoglucanase converts cellulose to cellobiose. On the contrary, the unbounded fraction of β-glucosidase converts cellobiose to glucose. This implies that the bound fraction of endoglucanase and exoglucanase plays a major role in cellobiose formation whereas, the free fraction of β-glucosidase is crucial in glucose formation. In addition to cellulose, the lignin present in the substrate can also bind to the hydrolytic enzymes and reduce the amount of the same available for cellulose hydrolysis. The adsorption step is followed by hydrolysis reaction which is inhibited by hydrolysis products like cellobiose, and glucose as well as degradation products from pretreatment like xylose, furfural. Apart from non-productive adsorption due to lignin and inhibition by products of hydrolysis and degradation products of pretreatment, the amount of enzyme also reduces due to deactivation by temperature. The deactivation temperature for a given enzyme is dependent on the source of the enzyme. Therefore, only the enzyme available after deactivation takes part in adsorption as well as hydrolysis reaction. Representing enzymatic hydrolysis of cellulose by a kinetic model is essential to study the performance of the hydrolysis process and improving the same. The kinetic model of cellulose hydrolysis is explained in section 3.

3. Kinetic modelling of cellulose hydrolysis

The semi-mechanistic model developed by Kadam et al. [8] is used in this study. This model is chosen because it is less complex than a mechanistic model and more reliable than an empirical model.