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# Validation of Inhibition Effects in the Cellulose Hydrolysis: A Dynamic Modelling Approach

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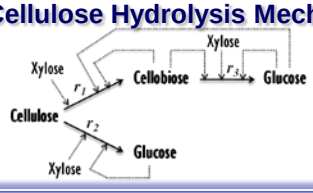
## I. Introduction

Enzymatic hydrolysis is one of the main steps in the processing of bioethanol from lignocellulosic raw materials. However, complete understanding of the underlying phenomena is still under development. Hence, this study has focused on validation of the inhibition effects in the cellulosic biomass hydrolysis employing a dynamic mathematical model. A systematic framework for parameter estimation is used for model validation, which helps to overcome the problem of parameter correlation. Data sets obtained from carefully designed enzymatic cellulose and cellobiose hydrolysis experiments, were used for parameter estimation (calibration) and validation purposes. The model predictions using calibrated parameters have shown good agreement with the validation data sets, which provides credibility to the model structure and the parameter values.

## II. Objective:

Validate the dynamic mathematical model for cellulosic biomass hydrolysis with particular focus on the validation of the hydrolysis and product inhibition mechanisms

## III. Cellulose Hydrolysis Mechanisms




## IV. Kinetics for Cellulose Hydrolysis (Kadam et al., 2004, Biotechnol Prog, 20, 698-705).

$$r_1 = \frac{k_{1r} E_{1B} R_S S}{1 + \frac{G_2}{K_{1IG2}} + \frac{G}{K_{1IG}} + \frac{X}{K_{1IX}}}$$

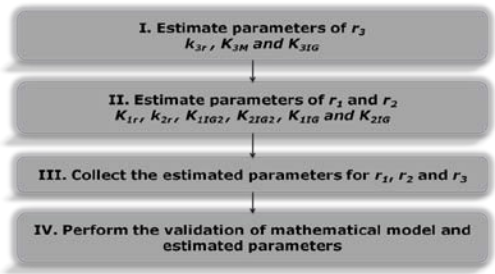
$$r_2 = \frac{k_{2r} \left(E_{1B} + E_{2B}\right) R_S S}{1 + \frac{G_2}{K_{2IG2}} + \frac{G}{K_{2IG}} + \frac{X}{K_{2IX}}}$$

$$r_3 = \frac{k_{3r} E_{2F} G_2}{K_{3M}\left(1 + \frac{G}{K_{3IG}} + \frac{X}{K_{3IX}}\right) + G_2}$$

## V. Datasets for Parameter Estimation

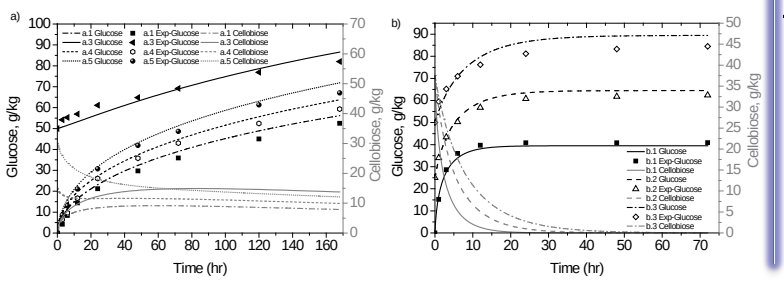
| | Substrate | Reaction | Enzyme | Enzyme Concentration (mg/g) | Inhibitor | No | Inhibitor concentration (g/kg) | Sampling time (hr) |
|---|---|---|---|---|---|---|---|---|
| Estimation | Avicel (100 g/kg) | $r_1 + r_2$ ($k_{1r}$, $k_{2r}$, $K_{1IG2}$, $K_{2IG2}$, $K_{1IG}$, $K_{2IG}$) | Celluclast 1.5L | 10.5 | No | a.1 | - | 0, 3, 6, 12, 24, 48, 72, 120, 168 |
| | | | | | Glucose | a.2 | 25 | |
| | | | | | | a.3 | 50 | |
| | | | | | Cellobiose | a.4 | 15 | |
| | | | | | | a.5 | 30 | |
| | Cellobiose (37.5 g/kg) | $r_3$ ($k_{3r}$, $K_{3M}$, $K_{3IG}$) | Novozymes 188 | 3.9 | No | b.1 | - | 0, 1, 3, 6, 12, 24, 48, 72 |
| | | | | | Glucose | b.2 | 25 | |
| | | | | | | b.3 | 50 | |

## VI. Systematic Framework for Parameter Estimation



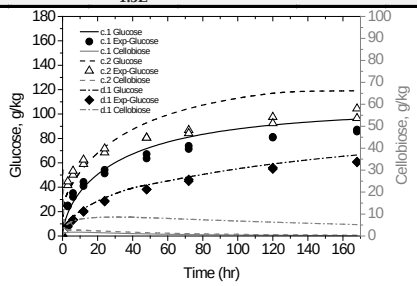

## VII. Results from Parameter Estimation

| Parameter | Value | Parameter | Value | Parameter | Value |
|---|---|---|---|---|---|
| $k_{1r}$, kg $g^{-1}h^{-1}$ | 22.3 | $k_{2r}$, kg $g^{-1}h^{-1}$ | 7.17 | $K_{3r}$, $h^{-1}$ | 263.9 |
| $K_{1IG2}$, g $kg^{-1}$ | 0.0035 | $K_{2IG2}$, g $kg^{-1}$ | 131.9 | $K_{3M}$, g $kg^{-1}$ | 0.0277 |
| $K_{1IG}$, g $kg^{-1}$ | 0.6494 | $K_{2IG}$, g $kg^{-1}$ | 0.019 | $K_{3IG}$, g $kg^{-1}$ | 0.0061 |




## VIII. Validation for Cellulose Hydrolysis

| | Substrate | Reaction | Enzyme | Enzyme Concentration (mg/g) | Inhibitor | No | Inhibitor concentration (g/kg) |
|---|---|---|---|---|---|---|---|
| Validation | Avicel (100 g/kg) | $r_1 + r_2 + r_3$ | Celluclast 1.5L + Novozyme 188 | 15.8 + 5.9 | No | c.1 | - |
| | | | | | Cellobiose | c.2 | 30 |
| | | $r_1 + r_2$ | Celluclast 1.5L | 21.1 | No | d.1 | - |




## IX. Discussion and Concluding Remarks

- This study has presented the validation of a mathematical model describing enzymatic hydrolysis of cellulose and including inhibition effects of products (cellobiose and glucose)
- The information obtained from the experiments has been used to first perform parameter estimation and then perform a model validation.
- A systematic approach for parameter estimation was introduced consisting of four main steps, to overcome the correlation issues of the parameters.
- The validation of the mathematical model has been performed using three different data sets, which have in general illustrated a good agreement between the model predictions and the experimental data. There are just a few exceptions where the model fit is less good: the model over-predicted product concentrations for an experimental data set where a high glucose concentration was present.
- An introduction of other inhibitory agents (i.e. xylose, furfural, etc.) present in the bioethanol production process, should also be taken into account in future experiments, in order to complete the analysis and understanding of the phenomena involved in the bioethanol production process.

## Acknowledgment

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*An extended version of this manuscript containing additional details is in preparation:*
*Tsai, C.-T., Morales-Rodriguez, R., Balduck, G., Gernaey, K.V., Meyer, A.S., Sin, G. (2011). A Dynamic Model for Cellulosic Biomass Hydrolysis: Validation of Hydrolysis and Product Inhibition Mechanism. To be submitted.*