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DYNAMIC SIMULATION, SENSITIVITY AND UNCERTAINTY ANALYSIS OF A DEMONSTRATION SCALE LIGNOCELLULOSIC ENZYMATIC HYDROLYSIS PROCESS

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Abstract

This study presents the uncertainty and sensitivity analysis of a lignocellulosic enzymatic hydrolysis model considering both model and feed parameters as sources of uncertainty. The dynamic model is parametrized for accommodating various types of biomass, and different enzymatic complexes, accounting a large number of parameters. The sensitivity analysis of model predictions with respect to model parameters is quantified by the delta mean square measure. By ranking the delta mean square, a reduced subset of parameters is found helping to identify the bottleneck of the model. The uncertainty analysis is carried for both model parameters and feed composition in order to assess the accuracy of the predictions. First, the model and feed parameters are sampled by Latin Hypercube Sampling (LHS) and then Monte Carlo simulations are run with the sampled values. Feed parameters are considered to be affected by non-zero mean noise because they are determined by a Near Infrared (NIR) instrument. LHS is performed on 2 parameters: the probability of the mean value and the probability of the standard deviation for each measurement. The Monte Carlo outputs are then analyzed by linear regression and the standardized regression coefficients (SRC) are computed for identifying the responsible parameters for model outputs precision. It is found that sugar yields are mostly sensitive to the composition of the enzymatic complex, and xylooligomers and glucose inhibition. pH is affected mostly by the amount of acetyl groups in the hemicellulose, while viscosity is sensitive to a few coefficients from its empirical equation.

Introduction

Biorefineries transform lignocellulosic agricultural wastes into products with higher added values following four major biochemical conversion steps: biomass pretreatment, enzymatic hydrolysis or liquefaction, fermentation, and purification [1]. Second generation bioethanol production technology had already reached commercial reality in 2012 [2] leading to the first plant commissioning in October 2013 by Beta Renewables in Crescentino, Italy [3], and followed by the first US plant named Project Liberty by POET-DSM, which started production in September 2014 in Iowa. Several other commercial size second generation bioethanol plants are expected to start operation in the near future: Abengoa Bioenergy (USA), DuPont (USA), Maabjerg Energy Concept (Denmark) etc.

During the pretreatment process, lignin is relocated and hemicellulose is partially hydrolyzed, allowing cellulose and the remaining hemicellulose to be exposed to enzymes for liquefaction. There are various types of pretreatment, out of which hydrothermal pretreatment with steam is seen as the best and cost-effective process [4], especially when the biorefinery is integrated with a power plant following the Integration Biomass Utilization System (IBUS) [1].

In the liquefaction phase, enzymes dissolve the pretreated lignocellulosic fibers in a high dry matter medium [5]. The enzymatic solution hydrolyses both hemicellulose and cellulose through a complex biochemical competitive conversion mechanism, which was thoroughly described and dynamically modeled in [6] with the following features: (1) Cellulose hydrolysis following the route: Cellulose \rightarrow Cellobiose \rightarrow Glucose and Cellulose \rightarrow Glucose; (2) Hemicellulose hydrolysis: Xylan \rightarrow Xylose; (3) Inhibition from sugar production; (4) Acetic acid production during hemicellulose hydrolysis; (5) Enzymatic complex

parametrization; (6) Plug flow transport phenomena for the first hours of liquefaction; (7) Suitable for continuous and batch reactors; (8) pH calculator; (9) Viscosity calculator; (10) pH and temperature dependency of reaction rates; (11) Langmuir type adsorption of enzymes onto solids.

The model from [6] was analyzed in a continuous demonstration scale reactor for the first 7 – 10 hours of liquefaction. In this new study the hemicellulose hydrolysis route is extended with xylooligomers production because of their strong inhibition capabilities [7]. The process is then analyzed in batch mode for 200 h of enzymatic hydrolysis. It is found that the sensitivity of model parameters change in time: in the first hours of liquefaction some reactions are more active than others, leading to a high sensitivity on endo-exo type cellulase, β -xylosidase, and xylooligomers inhibition; as liquefaction progresses, the xylooligomers pool is reduced and their inhibition becomes less important being replaced by glucose inhibition and xylooligomers hydrolysis.

The uncertainty of model predictions with respect to model parameters also change in time, i.e. a high uncertainty in the first hours of liquefaction, which is gradually reduced as substrates are consumed. The uncertainty with respect to feed parameters has an opposite behavior as it gradually increases as the hydrolysis process progresses.

Dynamic Simulation

Model parameters are set as in [8] and [6] with similar values for xylan to xylose conversion routes. A simulation is prepared for 200 h, which is higher than a normal enzymatic hydrolysis time. The initial conditions are listed in Table 1. In order to increase the cost efficiency of the process, liquefaction occurs at high dry matter values [5], i.e. 20 % to 40 %. In this simulation scenario, water content is set to 600 g/kg corresponding to a dry matter of 40 %. Fibers are soaked with acetic acid from the pretreatment process and base is added in order to bring the pH to the enzymatic optimal value of 5 units. The enzyme dosage or concentration corresponds to the optimal value indicated in [9], i.e. 4 g per 100 g of cellulose. It is assumed that the pretreated fibers have no sugar content, i.e. cellobiose, glucose, xylooligomers and xylose concentrations are set to 0. The hold-up of the batch reactor does not matter in this scenario because there are no inflows, nor outflows from the tank.

Table 1: Initial conditions for dynamic simulation. The enzyme dosage is set according to [9], i.e 4 g per 100 g of cellulose. The composition of water is set such that a dry matter of 40 % is obtained.

(a) Initial states.			(b) Dry matter, pH, and viscosity.		
State	Value	Unit	Calculated	Value	Unit
Cellulose	170	g/kg	Dry matter	40	%
Xylan	50	g/kg	pH	5	-
Lignin	140	g/kg	Viscosity	2.44	g/(ms)
Ash	10	g/kg			
Acid	7	g/kg			
Cellobiose	0	g/kg			
Glucose	0	g/kg			
Xylooligomers	0	g/kg			
Xylose	0	g/kg			
Furfural	4	g/kg			
Base	3	g/kg			
Enzymes	7	g/kg			
Water	600	g/kg			
Other	10	g/kg			

Figure 1 displays the simulation results: cellulose and xylan decomposition in the top left plot, glucose and xylose yields with intermediate cellobiose and xylooligomers in the right top plot, and pH,

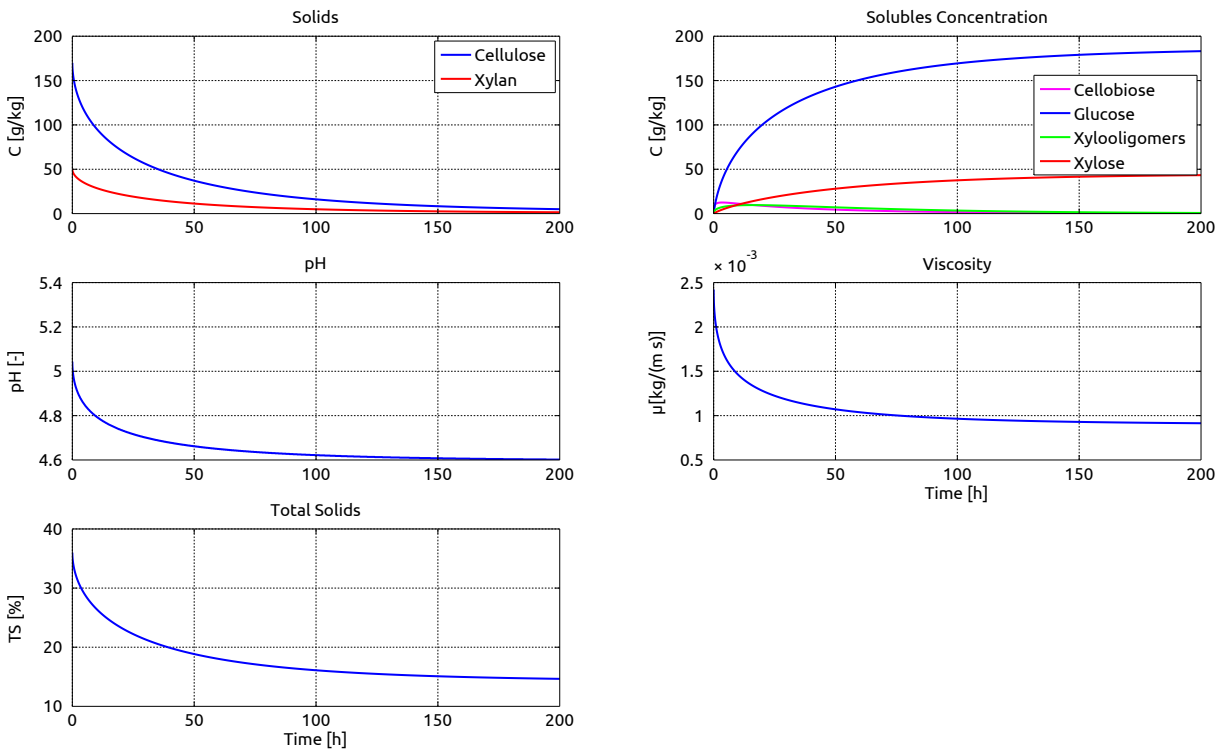


Figure 1: Dynamic simulation with model parameters from the literature.

viscosity and total solids in the remaining plots. Cellulose and xylan (solids) are hydrolyzed more rapidly in the first hours of liquefaction, and then all reaction rates gradually decrease due to product inhibition. Viscosity drops considerably in the first hours of liquefaction, from 2.5 g/(ms) to 1.5 g/(ms) after 10 h. pH also drops significantly in the first 10 h of liquefaction due to rapid xylan hydrolysis, which leads to acetic acid formation. In total, a drop of 0.4 pH units is recorded throughout the entire hydrolysis process. pH control would be necessary to keep the enzymatic activity close to optimality [10]. The solid content of the tank is reduced as cellulose and xylan get hydrolyzed. Lignin is not dissolved but rather only transported in solid state, so total solids cannot drop below 14%. Lignin is recovered in the distillation and separation phase of the refining process, and sent to an evaporation unit where it forms bio-pellets. These bio-pellets are then co-burnt with coal in a nearby power plant for steam generation.

Sensitivity Analysis

In [11] it is shown that the model formulated by Kadam in [8], which has fewer parameters and is the basis of the model in this study, is over-parametrized. Many of the parameters are not significant for predicting the model outputs because not all involved phenomena have the same importance. E.g., when using an enzymatic complex with a high concentration of β -glucosidase, cellobiose to glucose becomes dominant and cellobiose concentration remains low leading to a minimal inhibitory effect on the other reactions. In this case, all parameters referring to cellobiose inhibition are expected to have a low sensitivity on model outputs and could be discarded from the model or set to a fixed value. This was the case from [6]. More than that, because the concentration of cellobiose stays low, the entire state could be dropped, thus achieving a reduction in model order and complexity.

The sensitivity analysis helps process understanding by quantifying the relation between model outputs and parameters, and ranks all involved phenomena with respect to their importance. Identifying

a reduced subset of parameters also helps the model calibration procedure, which is computationally simplified and could run more often in a real industrial application.

The Delta Mean Square

A measure of sensitivity with respect to model parameters, and suitable for time varying signals, is the delta mean square δ_{ik}^{msqr} defined in [12]:

$$\delta_{ik}^{msqr} = \sqrt{\frac{1}{N} s_{nd,ik}^\top s_{nd,ik}} \quad (1)$$

where k is the parameter index, i is the model output index, N is the number of samples, and $s_{nd,ik}$ is a vector with the non dimensional sensitivity calculated in each sample:

$$s_{nd,ik} = \frac{\partial y_i}{\partial \theta_k} \frac{\theta_k}{sc_i} \quad (2)$$

$\partial y_i / \partial \theta_k$ represents the output variation with respect to a variation in parameter θ_k , and sc_i is a scaling factor with the same physical dimension as the corresponding observation in order to make this measure non dimensional. The scaling factor is chosen as the maximum value for that observation throughout the whole simulation time because some of the outputs, i.e. concentration of cellobiose and xylooligomers, are non-zero only throughout the first hours of liquefaction and a mean value would decrease their importance in a long simulation with many observation points:

$$sc_i = \max y_i(t) \quad (3)$$

All parameters are ranked according to δ_{ik}^{msqr} for each output i . As the sensitivity measure is non-dimensional, a cumulative variable is also defined as the sum of normalized sensitivities for a given parameter in all outputs. Because the model has to predict all defined outputs, the subset of significant parameters contains all parameters with a cumulative sensitivity above a threshold, which is set to 10 % of the maximum sensitivity.

Results

Figure 2 shows the sensitivity measure δ^{msqr} for cellobiose, glucose, xylooligomers and xylose. *Cellobiose sensitivity*: the most significant model parameters for cellobiose production are: β -glucosidase fraction from the enzymatic complex α_C^G ; cellobiose to glucose reaction rate parameters from r_3 , i.e. the reaction rate constant K_3 , the overall inhibition term I_3 , and glucose inhibition I_{G_3} ; cellulose to cellobiose reaction rate constant K_1 ; endo-exo type cellulase fraction from the enzymatic mix α_C^E ; and xylooligomers inhibition of r_1 , i.e. $I_{X_{O1}}$. These parameters are expected to affect cellobiose concentration as they appear either in cellobiose production r_1 or consumption r_3 . β -glucosidase fraction is the most important factor as it directly influences the pool of cellobiose. Only inhibition terms $I_{X_{O3}}$, I_{X_3} , I_{C_1} , I_{X_1} and I_{G_1} are not important in this scenario mostly because xylooligomers inhibition dominates in r_1 , and the overall inhibition term I_3 and glucose inhibition I_{G_3} are more significant than the other individual inhibition terms from r_3 .

Glucose sensitivity: glucose yield is sensitive to the following model parameters: cellulose to cellobiose reaction rate K_1 for creating a substrate for cellobiose to glucose reaction; fraction of exo-endo type cellulase α_C^E , which is directly involved in glucose production rates; xylooligomers inhibition $I_{X_{O1}}$, which strongly inhibits glucose production; β -xylosidase fraction α_X^X for contributing to xylooligomers production and consumption; xylooligomers to xylose reaction rate constant K_6 ; xylooligomers to xylose overall inhibition term I_6 ; glucose inhibition of xylooligomers reduction I_{G_6} . The xylooligomers to xylose

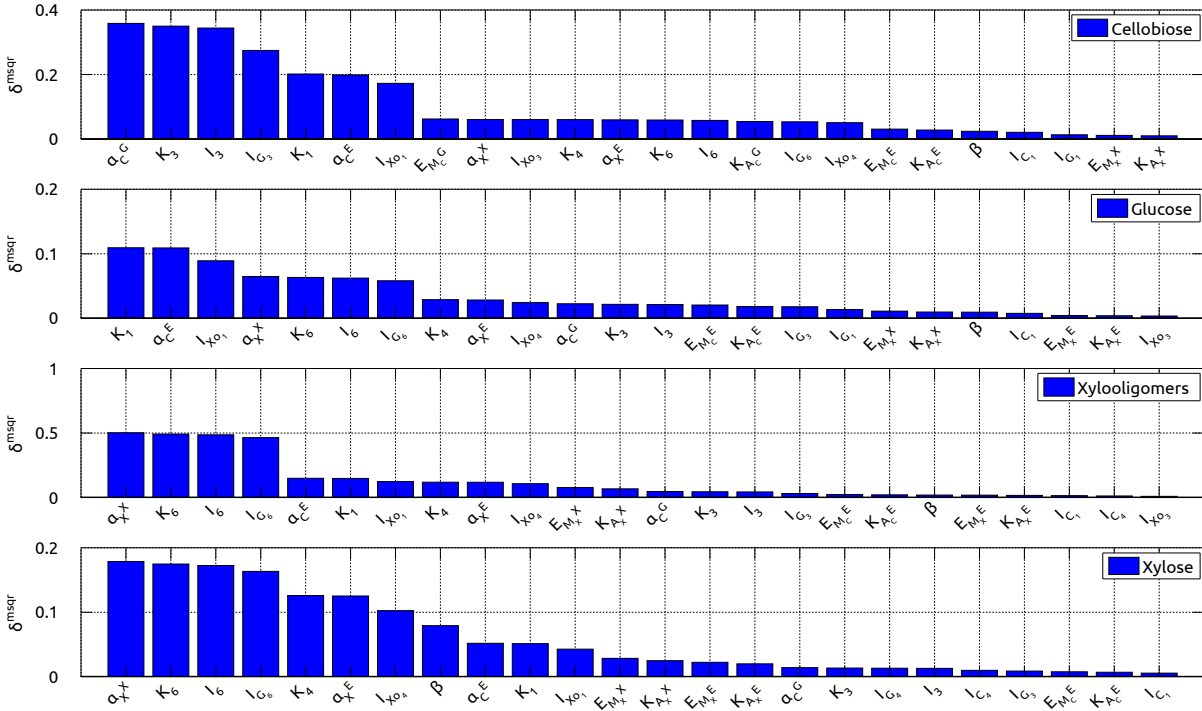


Figure 2: Sensitivity analysis: sorted δ_k^{msqr} for cellobiose, glucose, xylooligomers and xylose (top to bottom).

reaction parameters are important because they control the xylooligomers pool, which strongly inhibits glucose production, which is an important phenomena well captured by the model.

Xylooligomers sensitivity: the following model parameters are found to significantly influence xylooligomers production: xylooligomers to xylose parameters such as β -xylosidase fraction from the enzymatic complex α_X^X , the reaction rate constant K_6 , the overall inhibition term I_6 , and glucose inhibition I_{G_6} . β -xylosidase are directly involved in production and consumption of xylooligomers while the other parameters appear in the expression of r_6 , which determines consumption of xylooligomers.

Xylose sensitivity: xylose yield is sensitive to model parameters affecting xylooligomers to xylose, and xylan to xylooligomers reaction rates: β -xylosidase fraction α_X^X , reaction rate K_6 , the overall inhibition term I_6 , glucose inhibition I_{G_6} , reaction rate constant K_4 , endo-exo type xylanase α_X^E , xylooligomers inhibition I_{XO_4} , and β_{Ac} indirectly through pH dependency.

pH and viscosity sensitivities: are summarized in the first two plots from Figure 3. pH is mostly sensitive to the β parameter, as expected because it is an indication of the amount of acetyl groups in hemicellulose and their hydrolysis lead to acetic acid production. Viscosity μ is sensitive to coefficients a_4 , a_0 , a_1 and a_2 from the relative viscosity equation from [13].

The cumulative δ^{msqr} sensitivity measure is plotted in the bottom part of Figure 3. In order to predict glucose and xylose yields, the pH and the viscosity of the medium, only a subset of approximately 23 parameters could be used. Most of these parameters relate to enzymatic complex composition, i.e. the α parameters, xylooligomers to xylose, and cellobiose to glucose reaction rates, which makes sense since these intermediate products with a higher degree of polymerization represent a step towards xylose and glucose production, and also strongly inhibit sugar production. For predicting the pH and viscosity of the mixture, β_{Ac} , and a_0 , a_1 , a_2 , and a_4 would be enough.

This analysis identifies the bottleneck of the model predictions, i.e. the composition of the enzymatic complex and product inhibition, i.e. xylooligomers, cellobiose, glucose and xylose. The model can be reduced to 23 parameters and predict the sugar yields from the process, including pH and viscosity

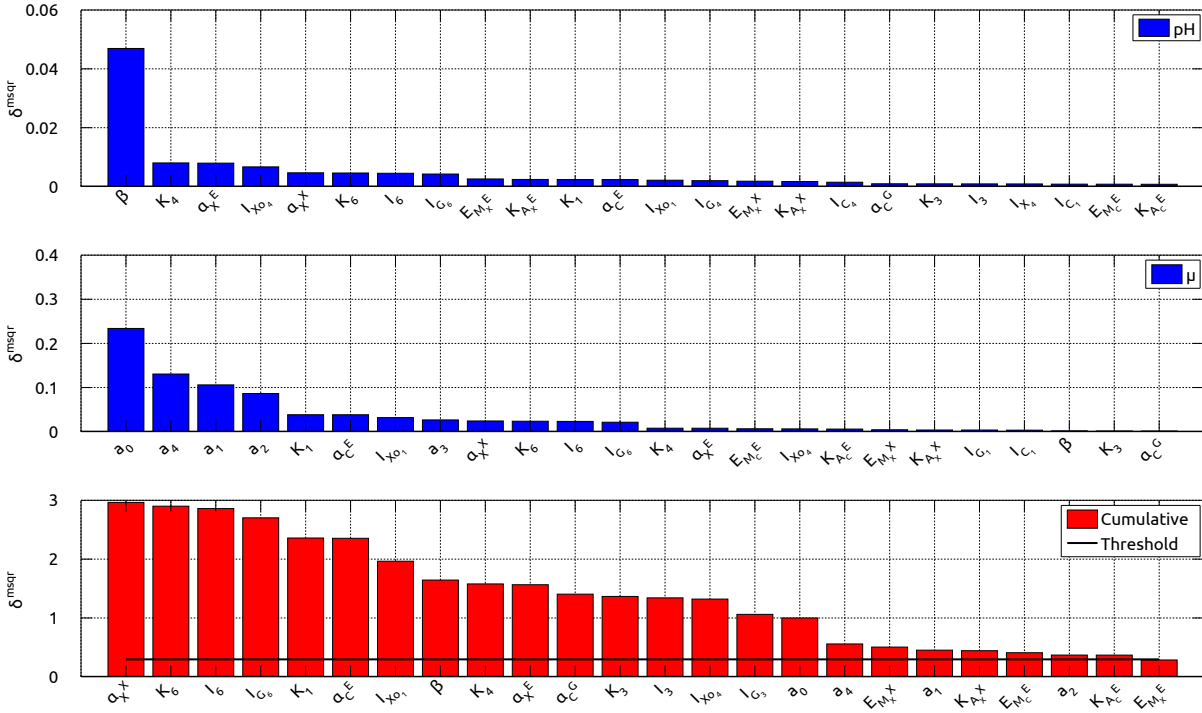


Figure 3: Sensitivity analysis: sorted δ_k^{msqr} for pH, viscosity and cumulative (top to bottom). The threshold indicates the most important parameter subset.

calculations.

Uncertainty Analysis of Model Predictions

The uncertainty analysis follows the standard Monte Carlo technique, which includes the following four steps [14]: (1) define parameters uncertainties with their range; (2) sampling of model and feed parameters using the Latin Hypercube Sampling technique (LHS); (3) run Monte Carlo simulations with sampled values; (4) evaluate results.

Sampling of Model and Feed Parameters

The uncertainty range for model parameters is based on expert information and is set to approximately 25 % like in [14]. Model parameters are considered uniformly distributed in the defined range. The feed parameters or the initial conditions for solids and acetic acid are typically measured with Near Infrared (NIR) equipment, which has a certain degree of uncertainty depending on how well the instrument is calibrated. This uncertainty is assumed to be normally distributed with mean value μ and standard deviation σ , such that it covers a range of 10 % uncertainty of nominal values:

$$\varepsilon \in N(\mu, \sigma) \quad (4)$$

where ε is the NIR measurement error, μ is the mean value and σ is the standard deviation. The mean value is assumed to be normally distributed while the standard deviation σ describes the measurement noise and is assumed to have a Gamma distribution parametrized in k and θ , i.e. a shape, and a scale parameter:

$$\mu \in N(0, \sigma_\mu) \quad \sigma \in \Gamma(1, 2) \quad (5)$$

where σ_μ is set to cover 10 % uncertainty of the nominal values listed in Table 1.

Model and feed parameters are treated separately in the uncertainty analysis because feed parameters can shadow the effects of model parameters uncertainty. When treating model parameters uncertainty, the feed parameters are set constant as in Table 1.

Uncertainty Analysis with Respect to Model Parameters

Figure 4(a) displays the results after 800 Monte-Carlo simulations with sampled model parameters and constant feed parameters. The patch area identifies the 5th-95th percentile interval. The model has a higher uncertainty between 10 h and 80 h for glucose, cellobiose, xylooligomers and xylose, and gradually decreases as cellulose and xylan are depleted. It is expected to have a reduced uncertainty on sugar production as the substrate is consumed, near the end of the hydrolysis time, and a higher uncertainty in the first hours of liquefaction when the competitive conversion mechanism with product inhibition is more active due to a higher concentration of xylooligomers and cellobiose. The uncertainty on pH slowly increases as hydrolysis progresses due to the uncertainty on the amount of acetyl groups in hemicellulose, expressed as the β_{Ac} parameter. However, at the end of the liquefaction process, the overall uncertainty on pH reaches 0.1 units, which is considered acceptable. The viscosity uncertainty is slightly higher in the first hours of liquefaction due to the uncertainty on the model parameters that affect cellulose and hemicellulose decomposition. As the amount of solids is reduced, the uncertainty interval also slowly decreases.

Uncertainty Analysis with Respect to Feed Parameters

The case with feed parameters uncertainty is shown in Figure 4(b). As expected, the uncertainty interval slowly increases as the hydrolysis process progresses. Glucose has the highest uncertainty due to a higher variation in the initial concentration of cellulose. A 10 % uncertainty on xylan content translates to little uncertainty on pH time profile, and to a smaller uncertainty on xylose final yield. β_{Ac} has a higher degree of uncertainty on pH than xylan variation. The viscosity is not affected much, being influenced mainly by the initial total solids composition, which appears as a slightly higher uncertainty interval in the first hours of liquefaction.

Sensitivity Analysis - The Standardized Regression Coefficients (SRC)

In the last step of the methodology, in addition to inference statistics, a sensitivity analysis is also performed using linear regression of Monte Carlo simulations outputs, also known as the standardized regression coefficients (SRC) [15]. The linear model from Equation (6) is fitted using the least squares method on the model outputs y , i.e. concentrations of glucose, cellobiose, xylose, xylooligomers, pH and viscosity, for each Monte Carlo simulation:

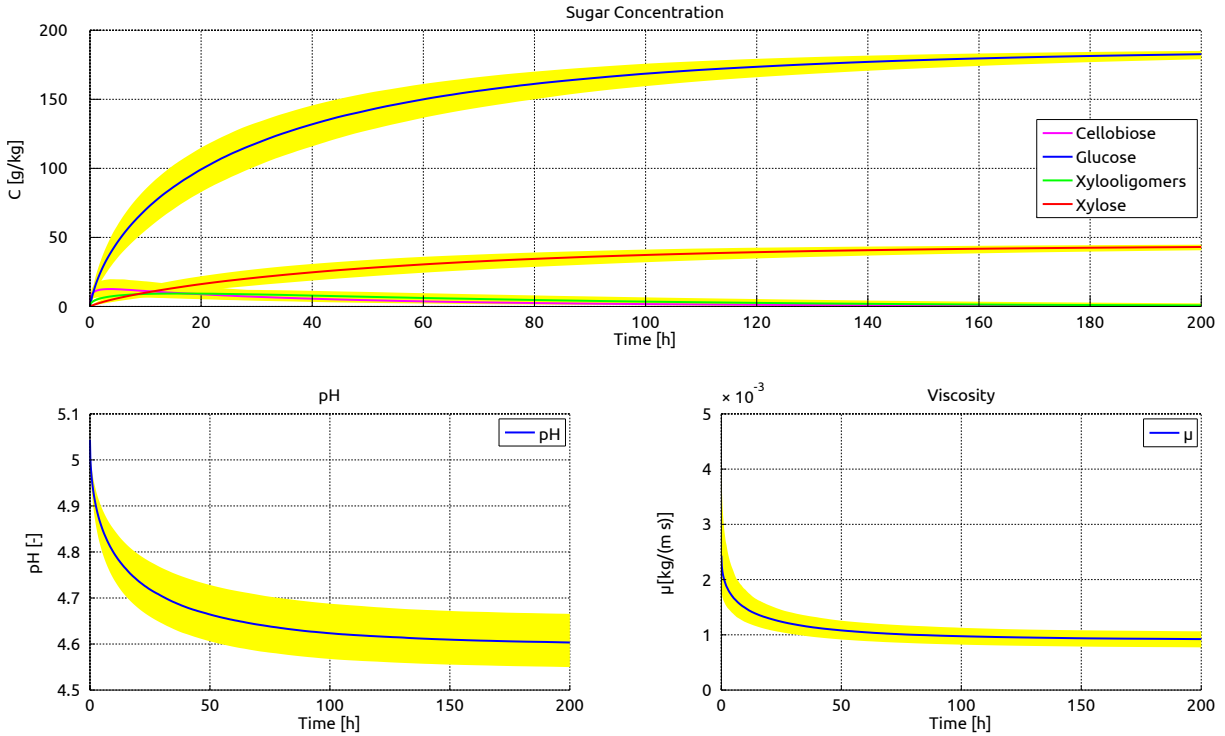
$$y_{jk} = a + \sum_i b_i \theta_{ji} \quad (6)$$

where y_{jk} is the j^{th} model output of simulation k , a and b_i are the linear model coefficients, and θ_{ji} is the i^{th} model parameter from the j^{th} sampled values.

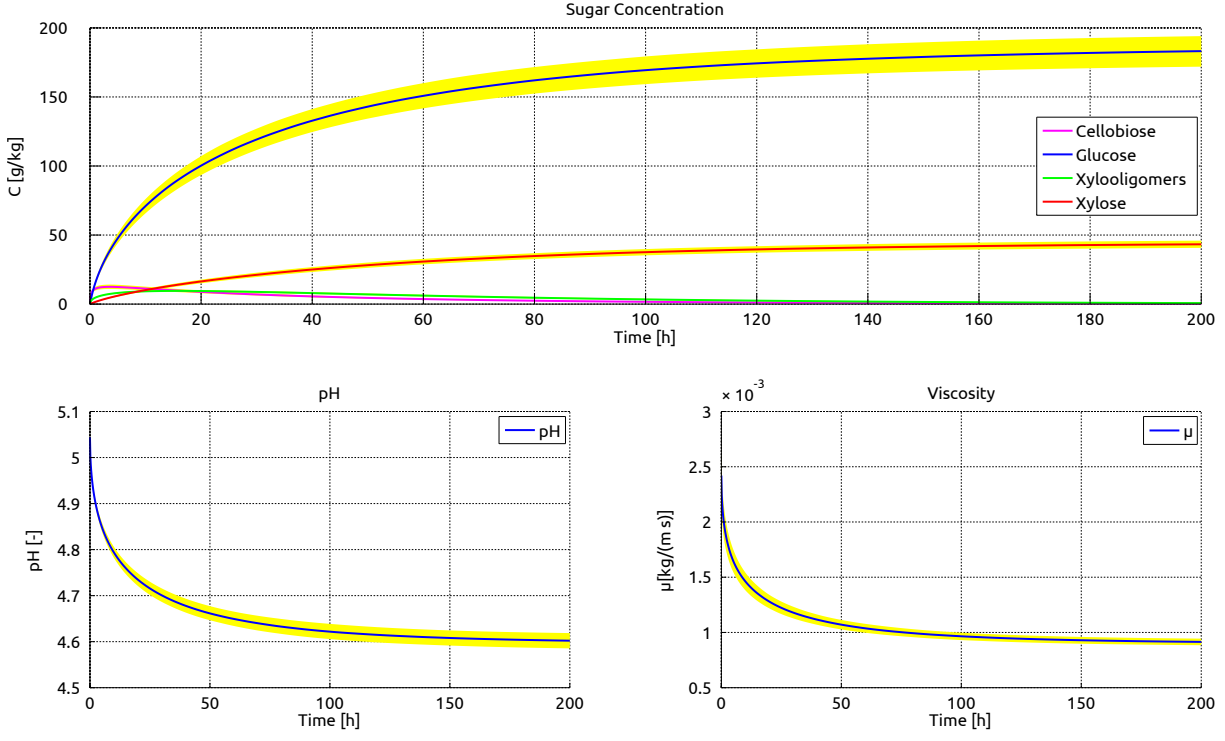
The methodology aims at finding how much each model parameter contributes to the variance or uncertainty recorded in the model predictions. The relation between parameter and output variations is quantified by the β coefficient defined as:

$$\beta = \frac{\sigma_{\theta_i}}{\sigma_y} b_i \quad (7)$$

The standardized regression coefficients with respect to model parameters are ranked in Table 2 at different time samples, i.e. 1 h, and 200 h. These tables suggest that the coefficients change in time, which is expected due to the xylooligomers and cellobiose intermediate products.



(a) Dynamic simulation with model parameters uncertainty. The patch area shows the 5th-95th percentile calculated after 800 Monte Carlo simulations.



(b) Dynamic simulation with feed parameters uncertainty. The patch area shows the 5th-95th percentile calculated after 800 Monte Carlo simulations.

Figure 4: Dynamic simulation with model and feed parameters uncertainty.

(a) SRC coefficients for model parameters uncertainty at $t = 1$ h.

θ	C_C	θ	C_G	θ	C_{Xo}	θ	C_X	θ	pH	θ	μ
α_C^E	0.48	α_C^E	0.45	K_4	0.58	α_X^X	0.41	β	-0.74	a_4	0.83
K_1	0.47	K_1	0.44	α_X^E	0.57	K_6	0.40	K_4	-0.40	a_2	0.20
I_{Xo_1}	0.38	I_{Xo_1}	0.34	I_{Xo_4}	0.47	I_6	-0.37	α_X^E	-0.39	a_0	0.20
α_C^G	-0.28	α_C^G	0.33	K_6	-0.22	α_X^E	0.33	I_{Xo_4}	-0.32	a_3	0.16
K_3	-0.27	K_3	0.32	α_X^X	-0.22	K_4	0.32	α_C^E	0.072	a_1	0.16

(b) SRC coefficients for model parameters uncertainty at $t = 200$ h.

θ	C_C	θ	C_G	θ	C_{Xo}	θ	C_X	θ	pH	θ	μ
K_3	-0.37	α_C^E	0.43	α_X^X	-0.48	β	-0.45	β	-0.99	a_0	0.91
α_C^G	-0.37	K_1	0.40	I_{G_6}	-0.46	α_X^X	0.38	K_4	-0.044	a_1	0.34
I_{G_3}	-0.36	α_X^X	0.39	K_6	-0.46	I_{G_6}	0.37	α_X^E	-0.040	a_2	0.20
I_3	0.34	K_6	0.37	I_6	0.43	K_6	0.36	α_X^X	-0.032	a_4	0.073
α_X^X	-0.30	I_6	-0.36	K_4	-0.14	I_6	-0.35	I_{G_6}	-0.030	α_X^X	-0.032

Table 2: Standardized regression coefficients (SRC) or β coefficients.

Table 2(a) shows the coefficients after 1 h of liquefaction. Cellulose and glucose concentrations are mostly sensitive to the fraction of endo-exo type of cellulase, which is expected since these enzymes directly contribute to cellulose depolymerization and glucose formation. The reaction rate constant K_1 for cellulose to cellobiose, and xylooligomers inhibition on the same reaction rate are also important. β -glucosidase, and reaction rate constant K_3 for cellulose to glucose have a slightly lower importance. Concentration of xylooligomers is mostly sensitive to endo-exo type of xylanase, reaction rate constant K_4 for xylan to xylooligomers, and xylooligomers inhibition term I_{Xo_4} . Concentration of xylose is influenced by β -xylosidase, reaction rate constant K_6 , and inhibition term I_6 . pH is mostly affected by the acetyl groups parameter β_{Ac} , while viscosity remains high and only a_4 is significant. These results show that the endo-exo type of enzymes from the enzymatic complex, as well as xylooligomers inhibition are important factors in the first hours of liquefaction.

In Table 2(b) it is seen that, as glucose inhibition becomes dominant mostly due to the fact that xylooligomers and cellobiose slowly drop in concentration, I_{G_6} is moving up the rankings of C_{Xo} and C_X . Enzymatic complex composition still remains in the first positions of the sensitivity rankings. pH remains sensitive to the acetyl groups concentration expressed in the β_{Ac} coefficient. As viscosity drops due to solids reduction, a_0 becomes the most significant parameter.

The standardized regression coefficients with respect to feed parameters are ranked in Table 3. Initial concentration of cellulose C_{C_s} is the most important parameter for cellobiose and glucose yields, which is expected. Initial concentration of xylan C_{X_s} is an important parameter for xylooligomers and xylose yields, as well as for the medium pH. Viscosity is sensitive to solid lignin C_{L_s} because lignin is neither produced, nor consumed during the hydrolysis process. A change in its concentration shifts the viscosity curve, directly affecting its value.

θ	C_C	θ	C_G	θ	C_{Xo}	θ	C_X	θ	pH	θ	μ
C_{C_S}	0.70	C_{C_S}	0.70	C_{X_S}	0.71	C_{X_S}	0.92	C_{X_S}	-0.99	C_{L_S}	0.57
C_W	-0.44	C_{X_S}	-0.49	C_{C_S}	0.33	C_{C_S}	-0.52	C_{C_S}	0.34	C_W	-0.39
C_{L_S}	-0.31	C_W	-0.41	C_{L_S}	-0.30	C_W	0.15	C_{L_S}	0.16	C_{X_S}	0.24
C_{X_S}	-0.18	C_{L_S}	-0.35	C_W	-0.28	C_{L_S}	-0.0081	C_W	0.064	C_{C_S}	0.10

Table 3: Standardized regression coefficients (SRC) or β coefficients for model output sensitivity with respect to feed parameters.

Conclusions

This report presents the sensitivity and uncertainty analysis of a liquefaction dynamic model. Two types of sensitivity analysis were conducted: one by calculating the delta mean square measure δ_{ik}^{msqr} for each output with respect to each model parameter; and another one by computing the standardized regression coefficients (SRC). Both analysis showed that the cellobiose, glucose, xylooligomers, and xylose, as well as the pH and viscosity of the medium are mostly sensitive to the enzymatic complex composition. Product inhibition by xylooligomers is mostly influential in the first hours of liquefaction, and as these high degree of polymerization sugars get depleted in time, glucose inhibition takes over. The model could be simplified to 23 parameters by choosing the most significant parameters above a threshold from the cumulative delta mean square measure.

The uncertainty analysis helped identifying the accuracy of the model considering 25 % uncertainty in model parameters and 10 % uncertainty in feed parameters. Model parameters uncertainty affects the process in its first hours and gradually decreases as the liquefaction progresses in time. Feed parameters had an opposite behavior, the uncertainty slowly increasing as the hydrolysis advanced in time.

This analysis is valuable for identifying and understanding the bottlenecks of a liquefaction process. The enzymatic complex should be identified prior to using the model in an industrial setup. The model could also be used to optimize the composition of the enzymatic solution, as well as the enzyme dosage. These issues are subject to future studies.

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