Model-based plant-wide optimization of large-scale lignocellulosic bioethanol plants.

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1. Introduction

This supplementary material summarizes the dynamic mathematical models for pretreatment, enzymatic hydrolysis and fermentation used in the plantwide optimization study. These models are necessary for calculating the steady state values for pretreatment and enzymatic hydrolysis, which are continuous processes, and the final states in fermentation, which is a batch process. Due to the high complexity and model nonlinearities, an analytical solution is difficult to derive. The alternative is to run a sufficiently long simulation with constant inputs and grab the stabilized or final state values.
This document also includes the correlation matrices used in Latin Hypercube Sampling of model parameters in the uncertainty analysis.

2. Mathematical Models

2.1. Pretreatment

The pretreatment process occurs in a large horizontal thermal reactor, which is pressurized with steam till the necessary reaction pressure/temperature. The following parameter distributed equation models the biomass transportation from inlet to outlet subject to conversion due to the steam temperature [1]:

\[
\frac{dC_k}{dt} = \frac{u_z}{\delta_z} (C_{k-1} - C_k) + R_k
\]  

(1)

\(C_k\) is the composition vector in central cell \(k\), \(C_{k-1}\) is the composition vector from the western neighbor, and \(R_k\) is the reaction rate vector from current cell \(k\).

Movement from west to east (left to right) is assumed.

The pretreatment conversion mechanism is shown in Figure 1. The reaction rates for building vector \(R_k\) are modeled as first order Arrhenius type reactions, and are detailed in [1]. A summary is given below:

Acetyls → Organic acids

Arabinan → Arabinose

Cellulose → Glucose → S-HMF

Xylan → Xylooligomers → Xylose

Pseudo-lignin

Furfural

Other degradation products

Figure 1: Hydrothermal pretreatment conversion mechanism [1].
• Glucose production due to cellulose hydrolysis:

$$r_G = k_G \exp \left( \frac{-E_G}{R \cdot T_K} \right) C_{CS} \quad (2)$$

where $k_G$ is the reaction rate constant, $E_G$ is the activation energy, and $C_{CS}$ is the cellulose in solid state. $R$ and $T_K$ are the universal gas constant, and the cell temperature in Kelvin degrees.

• 5-HMF production due to glucose degradation:

$$r_H = k_H \exp \left( \frac{-E_H}{R \cdot T_K} \right) C_G \quad (3)$$

where $C_G$ is the glucose concentration.

• Arabinan $C_{AS}$ is in low concentration and fully hydrolyzes to arabinose following the rate:

$$r_A = k_A \exp \left( \frac{-E_A}{R \cdot T_K} \right) C_{AS} \quad (4)$$

• Xylan is hydrolyzed having xylooligomers as an intermediate product:

$$r_{Xo} = k_{Xo} \exp \left( \frac{-E_{Xo}}{R \cdot T_K} \right) C_{XS} \quad (5)$$

where $C_{XS}$ is xylan in solid state.

• Xylooligomers are further decomposed into xylose:

$$r_X = k_X \exp \left( \frac{-E_X}{R \cdot T_K} \right) C_{Xo} \quad (6)$$

with $C_{Xo}$ as the concentration of xylooligomers.

• Xylose $C_X$ and arabinose $C_A$ are C5 sugars and can degrade into furfural:

$$r_F = k_F \exp \left( \frac{-E_F}{R \cdot T_K} \right) (C_X + C_A) \quad (7)$$

• Carbohydrates can react with inhibitors (furfural and 5-HMF) to create spherical droplets called pseudo-lignin [2]:

$$r_L = k_L \exp \left( \frac{-E_L}{R \cdot T_K} \right) (C_{Xo} + C_X + C_A + C_G)(C_F + C_H) \quad (8a)$$

3
\[ r_L = r_{L_X} + r_{L_X} + r_{L_A} + r_{L_G} \]  \hspace{1cm} (8b)

\[ r_L = r_{L_F} + r_{L_H} \]  \hspace{1cm} (8c)

\( r_{L_Xo}, r_{L_X}, r_{L_A}, \) and \( r_{L_G} \) show pseudo-lignin production due to xylooligomers, xylose, arabinose, and glucose participation expressed separately [1]:

\[ r_{L_Xo} = k_L \exp \left( -\frac{E_L}{R \cdot T_K} \right) C_{Xo}(C_F + C_H) \]  \hspace{1cm} (9a)

\[ r_{L_X} = k_L \exp \left( -\frac{E_L}{R \cdot T_K} \right) C_X(C_F + C_H) \]  \hspace{1cm} (9b)

\[ r_{L_A} = k_L \exp \left( -\frac{E_L}{R \cdot T_K} \right) C_A(C_F + C_H) \]  \hspace{1cm} (9c)

\[ r_{L_G} = k_L \exp \left( -\frac{E_L}{R \cdot T_K} \right) C_G(C_F + C_H) \]  \hspace{1cm} (9d)

\( r_{L_F} \) and \( r_{L_H} \) express pseudo-lignin production with furfural and 5-HMF participation [1]:

\[ r_{L_F} = k_L \exp \left( -\frac{E_L}{R \cdot T_K} \right) (C_{Xo} + C_X + C_A + C_G)C_F \]  \hspace{1cm} (10a)

\[ r_{L_H} = k_L \exp \left( -\frac{E_L}{R \cdot T_K} \right) (C_{Xo} + C_X + C_A + C_G)C_H \]  \hspace{1cm} (10b)

- Hemicellulose contains acetyl \( C_{AcS} \) that hydrolyze to produce acetic acid:

\[ r_{Ac} = k_{Ac} \exp \left( -\frac{E_{Ac}}{R \cdot T_K} \right) C_{AcS} \]  \hspace{1cm} (11)

The composition vector \( C_k \) and the reaction rate array \( R_k \) from Equation (1)
then become:

\[
C_k = \begin{bmatrix}
C_{C_S} \\
C_{X_S} \\
C_{A_S} \\
C_{L_S} \\
C_{A_{CS}} \\
C_{G} \\
C_{X_0} \\
C_{X} \\
C_{A} \\
C_{Ac} \\
C_{F} \\
C_{H} \\
C_{W} \\
C_{O}
\end{bmatrix}
\]

\[
R_k = \begin{bmatrix}
-r_G \\
-r_{X_0} \\
-r_{A} \\
r_L \\
-r_{Ac} \\
r_G - r_{O_G} - (1 - \alpha)r_{LG} \\
r_{X_0} - r_{X} - (1 - \alpha)r_{L_{X_0}} \\
r_{X} - r_{F_X} - r_{O_X} - (1 - \alpha)r_{L_X} \\
r_{A} - r_{O_A} - r_{F_{A}} - (1 - \alpha)r_{L_{A}} \\
r_{Ac} \\
r_{F} - \alpha r_{L_{F}} \\
r_{H} - \alpha r_{L_{H}} \\
0 \\
r_{O_X} + r_{O_G} + r_{O_A}
\end{bmatrix}
\] (12)

The mass balance is ensured by the following conditions:

\[
\sum R_k = 0 \text{g/(kgs)} \quad \sum C_k = 1000 \text{g/kg}
\] (13)

2.2. Enzymatic Hydrolysis

The enzymatic hydrolysis model has been formulated and analyzed in [3]. The competitive conversion routes are presented in Figure 2. The model has been extended in this study with enzyme deactivation in time as suggested by [4] plus enzymatic efficiency with respect to biomatrix opening described by the severity factor. A summary of the model equations is given next:

- The mass balance is built similarly to the thermal reactor case because the enzymatic hydrolysis runs at a very high initial dry matter, i.e. 40%. If Equation (1) is discretized into a single cell then it is equivalent to a continuous stirred tank reactor (CSTR). The enzymatic hydrolysis occurs in several tanks interconnected in series. In the first tank viscosity has a
Figure 2: Enzymatic hydrolysis conversion mechanism with inhibition. Extended from [3] with xylooligomers intermediate product, acetyl groups, and enzyme deactivation.
significant drop and is discretized in $N = 6$ cells, while the other tanks behave as CSTRs such that the retention time meets the 140 h constraint.

- The enzymatic solution parametrization:

$$C_E = C_{EC} + C_{EX}$$

(14)

The enzymatic solution contains cellulase $C_{EC}$ and xylanase $C_{EX}$. Cellulase is made up of endo-exo type cellulase $C_{EC}^{E}$ and $\beta$-glucosidase $C_{EC}^{G}$:

$$C_{EC} = C_{EC}^{E} + C_{EC}^{G}$$

(15)

Xylanase consists of exo-endo type xylanase $C_{EX}^{E}$ and xylosidase $C_{EX}^{X}$:

$$C_{EX} = C_{EX}^{E} + C_{EX}^{X}$$

(16)

The total concentration of enzymes can be parametrized using fractions:

$$C_E = \alpha_C^{E} C_{EC} + \alpha_G^{E} C_{EC} + \alpha_X^{E} C_{EC} + \alpha_X^{X}$$

(17)

where $\alpha_C^{E}$, $\alpha_G^{E}$, $\alpha_X^{E}$, and $\alpha_X^{X}$ are fractions of each type of cellulase and xylanase. Enzymes can be in two states: bounded or free. There is an equilibrium between the states described by:

$$C_{ECB}^{E} = E_{MC}^{E} \frac{K_{AC}^{E} C_{EC}^{E}}{1 + K_{AC}^{E} C_{ECB}^{E}} C_{S}$$

(18)

where $C_{ECB}^{E}$ are bounded exo-endo type cellulase, $C_{ECB}^{E}$ are free same type enzymes. $E_{MC}^{E}$ is a maximum adsorption term, and $K_{AC}$ the Langmuir adsorption constant. $C_{S}$ is the solid substrate that enzymes are bound to. Equation (18) applies to all types of enzymes, i.e. $\beta$-glucosidase, endo-exo type xylanase, and xylosidase.

- Kinetic modeling of the reaction rates from Figure 2

Reaction $r_1$ describes cellulose hydrolysis to cellobiose:

$$r_1 = \frac{K_1 \eta(T, pH, r) C_{ECB}^{E} C_{S}}{1 + \frac{C_{ECB}^{E}}{C_{I}^{C_1}} + \frac{C_{EXB}^{E}}{C_{I}^{X_1}} + \frac{C_{ECB}^{G}}{C_{I}^{G_1}} + \frac{C_{EXB}^{G}}{C_{I}^{X_1}} + \frac{C_{ECB}^{X}}{C_{I}^{X_1}}}$$

(19)
$K_1$ is the reaction rate, $\eta(T, p\text{H}, r)$ is the temperature, pH, and severity dependency of the enzymatic activity, $C_{E_{CB}}^E$ are the bounded exo-endo type cellulase, and $C_{CS}$ is the concentration of solid cellulose. The reaction rate is inhibited by cellobiose $C_C$, xylose $C_X$, xylooligomers $C_{Xo}$, and glucose $C_G$ through inhibition terms $I_{C_1}$, $I_{X_1}$, $I_{Xo_1}$, and $I_{G_1}$. In simultaneous saccharification and fermentation (SSF) ethanol also inhibits cellobiose formation [5] modeled through $I_{Eth_1}$ in the above rate.

Cellobiose decomposes to glucose by the action of both endo-exo type enzymes and $\beta$-glucosidase:

$$r_2 = \frac{K_2 \eta(T, p\text{H}, r) \left( C_{E_{CB}}^E + C_{E_{CB}}^G \right) C_{CS}}{1 + \frac{C_C}{I_{C_2}} + \frac{C_{Xo}}{I_{Xo_2}} + \frac{C_X}{I_{X_2}} + \frac{C_G}{I_{G_2}} + \frac{C_{Eth}}{I_{Eth_2}}}$$  \hspace{1cm} (20)

Cellobiose decomposes to glucose:

$$r_3 = \frac{K_3 \eta(T, p\text{H})C_{E_{CP}}^G C_C}{I_3 \left( 1 + \frac{C_{Xo}}{I_{Xo_3}} + \frac{C_X}{I_{X_3}} + \frac{C_G}{I_{G_3}} + \frac{C_{Eth}}{I_{Eth_3}} \right) + C_C}$$  \hspace{1cm} (21)

Xylan hydrolysis follows a similar path. Xylan form a xylooligomers pool:

$$r_4 = \frac{K_4 \eta(T, p\text{H})C_{E_{XB}}^E C_{XS}}{1 + \frac{C_C}{I_{C_4}} + \frac{C_{Xo}}{I_{Xo_4}} + \frac{C_X}{I_{X_4}} + \frac{C_G}{I_{G_4}} + \frac{C_{Eth}}{I_{Eth_4}}}$$  \hspace{1cm} (22)

Xylan could also be decomposed straight to xylose in a smaller amount:

$$r_5 = \frac{K_5 \eta(T, p\text{H}) \left( C_{E_{XB}}^E + C_{E_{XB}}^X \right) C_{XS}}{1 + \frac{C_C}{I_{C_5}} + \frac{C_{Xo}}{I_{Xo_5}} + \frac{C_X}{I_{X_5}} + \frac{C_G}{I_{G_5}} + \frac{C_{Eth}}{I_{Eth_5}}}$$  \hspace{1cm} (23)

Xylooligomers are further decomposed to xylose:

$$r_6 = \frac{K_6 \eta(T, p\text{H})C_{E_{XF}}^X C_{Xo}}{I_6 \left( 1 + \frac{C_C}{I_{C_6}} + \frac{C_X}{I_{X_6}} + \frac{C_G}{I_{G_6}} + \frac{C_{Eth}}{I_{Eth_6}} \right) + C_{Xo}}$$  \hspace{1cm} (24)

Acetic acid production happens due to acetyl being released along with xylan hydrolysis:

$$r_7 = \beta_{Ac}(r_4 + r_5)$$  \hspace{1cm} (25)
Enzymes deactivate in time due to thermal inactivation and exposure to ethanol \([4]\):

\[ r_8 = -K_8 C_E^2 \]  \(26\)

- pH is modeled based on the charge balance equation:

\[ [H^+] - [OH^-] - [Ac^-] + [Na^+] = 0 \]  \(27\)

The hydrogen ion concentration is found as the solution to the charge balance equation. The other ions are expressed using the states and dissociation constants. pH is then defined as:

\[ pH = -\log_{10}[H^+] \]  \(28\)

- The enzymatic activity is a function of temperature, pH and severity factor as illustrated in Figure 3:

\[ \eta(T, pH, r) = \eta_T(T)\eta_p(pH)\eta_r(r) \]  \(29\)

The temperature and pH dependency are determined based on linear interpolation of experimental tabular data, and have the shape of a bell with a single optimal peak \([6, 7]\). The severity \([8, 9]\) dependency illustrate the biomatrix opening, and models how hard the enzymes can access the cellulosic and hemicellulosic fibers due to the physical structure of the biomass. The severity factor is a function of retention time and temperature \([8]\). Insufficient pretreatment can block enzymes accessibility to fibers.
Figure 3: Enzymatic activity dependency on temperature, pH, and severity factor $r$.

The composition vector $C_k$ and the reaction rates array $R_k$ are shown next:

$$
C_k = \begin{bmatrix}
C_{CS} \\
C_{XS} \\
C_{LS} \\
C_{AC} \\
C_{Ac} \\
C_{C} \\
C_{G} \\
C_{Xo} \\
C_{X} \\
C_{F} \\
C_{H} \\
C_{B} \\
C_{E} \\
C_{W} \\
C_{O}
\end{bmatrix}
$$

$$
R_k = \begin{bmatrix}
-r_1 - r_2 \\
-r_4 - r_5 \\
0 \\
-r_7 \\
r_1 - r_3 \\
r_2 + r_3 \\
r_4 - r_6 \\
r_5 + r_6 \\
r_7 \\
0 \\
0 \\
0 \\
-r_8 \\
0 \\
0
\end{bmatrix}
$$

Conservation of mass is ensured by the following conditions:

$$
\sum R_k = 0 \text{g/(kgs)} \quad \sum C_k = 1000 \text{g/kg}
$$

(30)
2.3. C5 and C6 Co-Fermentation Model

The fermentation tank is modeled as a continuous stirred tank reactor (CSTR) with reaction kinetics derived from [10]. Since it can take 70 h for filling the tank, it is important to track the total mass change in time:

\[
\frac{dM_f}{dt} = F_{in,f} - F_{out,f}
\]  

(32)

where \(M_f\) is the fermenter hold-up in kg, and \(F_{in,f}\) and \(F_{out,f}\) are the mass inflow and outflow rates in kg/s.

Component composition is tracked with the following equation for variable hold-up:

\[
\frac{d(C_f M_f)}{dt} = F_{in,f} C_{in,f} - F_{out,f} C_f + R_f M_f
\]  

(33)

where \(C_f\) is the composition vector in g/kg, \(C_{in,f}\) is the inflow composition of liquefied fibers coming from the enzymatic hydrolysis process, and \(R_f\) is the reaction rate vector in g/(kgs).

Substituting Equation (32) into (33) yields:

\[
\frac{dC_f}{dt} = \frac{1}{M_f} \left[ F_{in,f} (C_{in,f} - C_f) \right] + R_f
\]  

(34)

The reaction rates are calculated using standard global black box model to represent fermentation activity [11]:

- Glucose uptake:

\[
R_G = -q_{G_{1}}
\]  

(35)

where \(R_G\) is the glucose uptake rate, and equals the glucose consumption rate with inhibition \(q_{G_{1}}\), which is calculated as follows:

\[
q_{G_{1}} = \frac{1}{Y_{Eth_G}} q_{Eth_{G_{1}}}
\]  

(36)

\(Y_{Eth_G}\) is the yield parameter for ethanol production from glucose. \(q_{Eth_{G_{1}}}\) represents ethanol production rate from glucose with inhibition:

\[
q_{Eth_{G_{1}}} = q_{Eth_G} \cdot I_{Eth_G} \cdot I_{F_G} \cdot I_{A_G} \cdot I_{HMF_G}
\]  

(37)
$q_{EthG}$ is ethanol production from glucose only with substrate inhibition, while $I_{EthG}$, $I_{FG}$, $I_{AG}$, and $I_{HMF}$ are inhibitory terms for ethanol (product inhibition), furfural, acetate, and 5-HMF respectively. $q_{EthG}$ is modeled as in [12] with pH dependency extension:

$$q_{EthG} = q_{MaxG}(pH) \cdot \frac{C_G}{C_{Cell}K_{SPG} + C_G + \frac{C_G^2}{K_{IPG}}}$$  \hspace{1cm} (38)

where $C_G$ and $C_{Cell}$ are glucose and cell biomass concentrations, and $K_{SPG}$ and $K_{IPG}$ are glucose self-inhibition terms.

The pH dependency is built empirically to resemble a bell with $q_{MaxG}$ as peak:

$$q_{MaxG}(pH) = q_{MaxG} \frac{K_{0G}}{\left(1 + \frac{10^{pH}}{K_{1G}} + \frac{K_{2G}}{10^{pH}}\right)^{-1}}$$  \hspace{1cm} (39)

where $K_{0G}$, $K_{1G}$, and $K_{2G}$ parametrize the shape of the bell.

Ethanol inhibition on glucose uptake or product inhibition has been defined in [12]:

$$I_{EthG} = 1 - \left(\frac{C_{Eth}}{P_{MPG}}\right)^{\gamma_G}$$  \hspace{1cm} (40)

with $P_{MPG}$ and $\gamma_G$ as parameters. $C_{Eth}$ is the concentration of ethanol.

Furfural, acetate and 5-HMF inhibition are modeled as below:

$$I_i = \frac{K_{iG}}{K_{iG} + C_i}$$  \hspace{1cm} (41)

where $I_i$ is the inhibition from component $i$, $K_{iG}$ is the inhibitory constant, and $C_i$ is the concentration. Index $i$ can be $\{F, Ac, HMF\}$ signifying furfural, acetate, or 5-HMF.

- Xylose uptake follows the same equation structure as glucose uptake but with different parameter values:

$$R_X = -q_{Xj}$$  \hspace{1cm} (42)
Xylose consumption with inhibition is calculated based on ethanol production from xylose \( q_{Eth,X} \) with inhibition, and yield parameter \( Y_{Eth,X} \):

\[
q_{X,I} = \frac{1}{Y_{Eth,X}} q_{Eth,X}
\]  (43)

Ethanol production from xylose comprises inhibition terms from product \( I_{Eth,X} \), furfural \( I_{F,X} \), acetate \( I_{Ac,X} \), and 5-HMF \( I_{HMF,X} \):

\[
q_{Eth,X,I} = q_{Eth,X} \cdot I_{Eth,X} \cdot I_{F,X} \cdot I_{Ac,X} \cdot I_{HMF,X}
\]  (44)

\( q_{Eth,X} \) shows ethanol production with substrate inhibition modeled as in [12] with pH dependency extension:

\[
q_{Eth,X} = q_{Max,X}(pH) \cdot C_{Cell} \frac{C_X}{K_{SP,X} + C_X + \frac{C_X^2}{K_{IP,X}}}
\]  (45)

\( C_X \) and \( C_{Cell} \) are xylose and cell biomass concentrations, while \( K_{SP,X} \) and \( K_{IP,X} \) are xylose inhibitory parameters.

The pH dependency curve is parametrized in \( K_{0,X}, K_{1,X}, \) and \( K_{2,X} \) with \( q_{Max,X} \) as peak:

\[
q_{Max,X}(pH) = q_{Max,X} \frac{K_{0,X}}{\left(1 + \frac{10^{pH}}{K_{K_1,X}} + \frac{K_{2,X}}{10^{pH}}\right)}
\]  (46)

Product inhibition is similar to the glucose case with parameters for xylose \( P_{MP,X} \) and \( \gamma_X \):

\[
I_{Eth,X} = 1 - \left(\frac{C_{Eth}}{P_{MP,X}}\right)^{\gamma_X}
\]  (47)

Furfural, acetate and 5-HMF inhibition have the following equations:

\[
I_{i,X} = \frac{K_{i,X}}{K_{i,X} + C_i}
\]  (48)

with index \( i \in \{F, Ac, HMF\} \).
• Ethanol production is the sum between the rates from glucose and xylose uptake shown in Equations (36) and (43):

\[ R_{Eth} = q_{G1} + q_{X1} \]  
(49)

• Furfural uptake rate \( R_F \) is calculated as:

\[ R_F = -q_F \]  
(50)

\[ q_F = q_{MaxF} C_{Cell} \frac{C_F}{K_{F2} + C_F} \]  
(51)

where \( q_{MaxF} \) is the maximum uptake rate, \( C_{Cell} \) is the cell biomass concentration and \( K_{F2} \) is a substrate inhibition parameter.

• 5-HMF uptake is modeled similarly as in the furfural case with an inhibitory term addition due to furfural:

\[ R_{HMF} = -q_{HMF1} \]  
(52)

\[ q_{HMF1} = q_{HMF} \cdot I_{F_{HMF}} \]  
(53)

\[ q_{HMF} = q_{MaxHMF} C_{Cell} \frac{C_{HMF}}{C_{HMF} + K_{HMF2}} \]  
(54)

\[ I_{F_{HMF}} = \frac{K_I_{HMF}}{K_I_{HMF} + C_F} \]  
(55)

where \( K_{HMF2} \) and \( K_I_{HMF} \) are inhibition parameters.

• Acetate uptake and production:

\[ R_{Ac} = q_{Ac_{HMF}} - q_{Ac} \]  
(56)

where \( q_{Ac_{HMF}} \) is the production rate and \( q_{Ac} \) is the uptake rate. The acetate production rate is calculated based on Equation (53) and the yield parameter \( Y_{Ac_{HMF}} \):

\[ q_{Ac_{HMF}} = q_{HMF1} \cdot Y_{Ac_{HMF}} \]  
(57)
Acetate uptake is modeled similarly to 5-HMF uptake:

$$q_{Ac} = q_{Max,Ac} \frac{C_{Ac}}{C_{Ac} + K_{Ac,S}}$$  \hspace{1cm} (58)$$

with $q_{Max,Ac}$ as maximum uptake rate and $K_{Ac,S}$ as substrate inhibition term.

- CO₂ production occurs in glucose, xylose and acetate uptake:

$$R_G = q_{G,I} Y_{G} + q_{X,I} Y_{X} + q_{Ac,Y} Y_{Ac}$$  \hspace{1cm} (59)$$

where $Y_{G}$, $Y_{X}$ and $Y_{Ac}$ are yield parameters.

- Cell biomass growth is modeled as in [12]:

$$R_{Cell} = \mu_T$$  \hspace{1cm} (60)$$

where $\mu_T$ is the specific growth of C5 and C6 mixture detailed as follows:

$$\mu_T = \frac{C_G}{C_G + C_X} \mu_G + \frac{C_X}{C_G + C_X} \mu_X$$  \hspace{1cm} (61)$$

$\mu_G$ and $\mu_X$ are the specific growths on glucose and xylose:

$$\mu_G = (q_{G,I} - m_G C_{Cell}) Y_{Cell_G}$$  \hspace{1cm} (62)$$

$$\mu_X = (q_{X,I} - m_X C_{Cell}) Y_{Cell_X}$$  \hspace{1cm} (63)$$

$m_G$ and $m_X$ are maintenance coefficients for glucose and xylose, while $Y_{Cell_G}$ and $Y_{Cell_X}$ are yield parameters.

3. Model Parameters

Table[1] from the supplementary material indicates the values with units for all parameters used in the mathematical models described before. The table is split into pretreatment, enzymatic hydrolysis and fermentation. The model parameter values are taken from [1] (pretreatment), [3] (enzymatic hydrolysis) and [10] (C5 and C6 co-fermentation).
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<th>Value</th>
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<td>Xylose reaction constant</td>
<td>( 1.31 \times 10^{-34} )</td>
<td>1/s</td>
</tr>
<tr>
<td>11 ( k_G )</td>
<td>Glucose reaction constant</td>
<td>( 1.11 \times 10^{-35} )</td>
<td>1/s</td>
</tr>
<tr>
<td>12 ( k_{PL} )</td>
<td>Pseudo-lignin reaction constant</td>
<td>( 1.03 \times 10^{-33} )</td>
<td>1/s</td>
</tr>
<tr>
<td>13 ( k_F )</td>
<td>Furfural reaction constant</td>
<td>( 5.09 \times 10^{-33} )</td>
<td>1/s</td>
</tr>
<tr>
<td>14 ( k_{HMF} )</td>
<td>5-HMF reaction constant</td>
<td>( 1 \times 10^{-31} )</td>
<td>1/s</td>
</tr>
<tr>
<td>15 ( k_{Ac} )</td>
<td>Organic acid reaction constant</td>
<td>( 4.88 \times 10^{-24} )</td>
<td>1/s</td>
</tr>
<tr>
<td>16 ( k_A )</td>
<td>Arabinose reaction constant</td>
<td>106 225</td>
<td>1/s</td>
</tr>
<tr>
<td>17 ( \alpha_{PL} )</td>
<td>Pseudo-lignin and inhibitors fraction</td>
<td>0.1019</td>
<td>–</td>
</tr>
</tbody>
</table>

<p>| ( K_1 ) | Cellulose to cellobiose reaction constant | 0.005 916 | kg/(gs) |
| 22 ( K_2 ) | Cellulose to glucose reaction constant | 0.006 507 5 | kg/(gs) |
| 23 ( K_3 ) | Cellobiose to glucose reaction constant | 0.005 522 7 | kg/(gs) |
| 24 ( K_4 ) | Xylan to xylooligomers reaction constant | 0.002 002 6 | kg/(gs) |
| 25 ( K_5 ) | Xylan to xylose reaction constant | 0.003 393 6 | kg/(gs) |
| 26 ( K_6 ) | Xylooligomers to xylose reaction constant | 0.002 822 8 | kg/(gs) |</p>
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<tr>
<th></th>
<th>Description</th>
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<tbody>
<tr>
<td>28</td>
<td>$K_7$ Enzyme deactivation reaction constant</td>
<td>$2.5 \times 10^{-7}$ kg/(gs)</td>
</tr>
<tr>
<td>29</td>
<td>$K_{AC}^E$ Exo-endo cellulase Langmuir adsorption constant</td>
<td>$1.0444$</td>
</tr>
<tr>
<td>30</td>
<td>$K_{AX}^E$ Exo-end xylanase Langmuir adsorption constant</td>
<td>$0.3784$</td>
</tr>
<tr>
<td>31</td>
<td>$K_{AC}^G$ $\beta$-glucosidase Langmuir adsorption constant</td>
<td>$0.056976$</td>
</tr>
<tr>
<td>32</td>
<td>$K_{AX}^G$ Xilosidase Langmuir adsorption constant</td>
<td>$0.093253$</td>
</tr>
<tr>
<td>33</td>
<td>$E_{MC}^E$ Maximum exo-end cellulase adsorption</td>
<td>$0.016042$</td>
</tr>
<tr>
<td>34</td>
<td>$E_{MC}^G$ Maximum $\beta$-glucosidase adsorption</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>35</td>
<td>$E_{MX}^E$ Maximum endo-exo xylanase adsorption</td>
<td>$0.38978$</td>
</tr>
<tr>
<td>36</td>
<td>$E_{MX}^G$ Maximum xyloligosidase adsorption</td>
<td>$0.51178$</td>
</tr>
<tr>
<td>37</td>
<td>$I_{C1}$ Cellobiose inhibition on $r_1$</td>
<td>$0.02014$</td>
</tr>
<tr>
<td>38</td>
<td>$I_{G1}$ Glucose inhibition on $r_1$</td>
<td>$0.10255$</td>
</tr>
<tr>
<td>39</td>
<td>$I_{Xo1}$ Xylooligomers inhibition on $r_1$</td>
<td>$0.0078145$</td>
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<tr>
<td>40</td>
<td>$I_{X1}$ Xylose inhibition on $r_1$</td>
<td>$0.01503$</td>
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<tr>
<td>41</td>
<td>$I_{Eth1}$ Ethanol inhibition on $r_1$</td>
<td>$0.15$</td>
</tr>
<tr>
<td>42</td>
<td>$I_{C2}$ Cellobiose inhibition on $r_2$</td>
<td>$69.539$</td>
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<tr>
<td>43</td>
<td>$I_{G2}$ Glucose inhibition on $r_2$</td>
<td>$0.067554$</td>
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<tr>
<td>44</td>
<td>$I_{Xo2}$ Xylooligomers inhibition on $r_2$</td>
<td>$0.059612$</td>
</tr>
<tr>
<td>45</td>
<td>$I_{X2}$ Xylose inhibition on $r_2$</td>
<td>$0.14843$</td>
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<tr>
<td>46</td>
<td>$I_{G3}$ Glucose inhibition on $r_3$</td>
<td>$8.7211$</td>
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<tr>
<td>47</td>
<td>$I_{Xo3}$ Xylooligomers inhibition on $r_3$</td>
<td>$111.6822$</td>
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<tr>
<td>48</td>
<td>$I_{X3}$ Xylose inhibition on $r_3$</td>
<td>$210.1911$</td>
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<td>49</td>
<td>$I_{O3}$ Overall inhibition on $r_3$</td>
<td>$15.949$</td>
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<tr>
<td>50</td>
<td>$I_{C4}$ Cellobiose inhibition on $r_4$</td>
<td>$53.4804$</td>
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<tr>
<td>51</td>
<td>$I_{G4}$ Glucose inhibition on $r_4$</td>
<td>$2.0899$</td>
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<tr>
<td>52</td>
<td>$I_{Xo4}$ Xylooligomers inhibition on $r_4$</td>
<td>$113.4492$</td>
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<td>53</td>
<td>$I_{X4}$ Xylose inhibition on $r_4$</td>
<td>$233.0874$</td>
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<td>54</td>
<td>$I_{C5}$ Cellobiose inhibition on $r_5$</td>
<td>$2.7413$</td>
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<td>55</td>
<td>$I_{G5}$ Glucose inhibition on $r_5$</td>
<td>$4.7951$</td>
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<tr>
<td>56</td>
<td>$I_{Xo5}$ Xylooligomers inhibition on $r_5$</td>
<td>$83.5479$</td>
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<td>57</td>
<td>$I_{X5}$ Xylose inhibition on $r_5$</td>
<td>$271.2334$</td>
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<tr>
<td>58</td>
<td>$I_{C6}$ Cellobiose inhibition on $r_6$</td>
<td>$46.9663$</td>
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<tr>
<td>59</td>
<td>$I_{G6}$ Glucose inhibition on $r_6$</td>
<td>$3.0412$</td>
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<td>60</td>
<td>$I_{X6}$ Xylose inhibition on $r_6$</td>
<td>$198.3351$</td>
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<tr>
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<td>Value</td>
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<tr>
<td>61</td>
<td>Overall inhibition on $r_6$</td>
<td>28.2079 g/kg</td>
</tr>
<tr>
<td>62</td>
<td>Severity dependency</td>
<td>9 –</td>
</tr>
<tr>
<td>63</td>
<td>Severity dependency</td>
<td>2.915 –</td>
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<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>64</td>
<td>$Y_{CO_2G}$ CO$_2$ production from glucose uptake</td>
<td>0.47 kg/kg</td>
</tr>
<tr>
<td>65</td>
<td>$Y_{CO_2X}$ CO$_2$ production from xylose uptake</td>
<td>0.4 kg/kg</td>
</tr>
<tr>
<td>66</td>
<td>$K_{FS}$ Furfural uptake self inhibition constant</td>
<td>0.05 g/kg</td>
</tr>
<tr>
<td>67</td>
<td>$K_{IFG}$ Glucose inhibition on furfural uptake</td>
<td>0.75 g/kg</td>
</tr>
<tr>
<td>68</td>
<td>$K_{IHMFF}$ Furfural inhibition on 5-HMF uptake</td>
<td>0.25 g/kg</td>
</tr>
<tr>
<td>69</td>
<td>$K_{IFX}$ Xylose inhibition on furfural uptake</td>
<td>0.35 g/kg</td>
</tr>
<tr>
<td>70</td>
<td>$q_{F_{\text{Max}}}$ Maximum furfural uptake</td>
<td>$4.6706 \times 10^{-5}$ 1/s</td>
</tr>
<tr>
<td>71</td>
<td>$K_{IPG}$ Glucose uptake self inhibition parameter</td>
<td>4890 g/kg</td>
</tr>
<tr>
<td>72</td>
<td>$K_{ISP}$ Glucose uptake self inhibition parameter</td>
<td>1.342 g/kg</td>
</tr>
<tr>
<td>73</td>
<td>$P_{MPG}$ Ethanol inhibition on glucose uptake</td>
<td>103 g/kg</td>
</tr>
<tr>
<td>74</td>
<td>$\gamma_{G}$ Ethanol inhibition on glucose uptake</td>
<td>1.42 –</td>
</tr>
<tr>
<td>75</td>
<td>$Y_{EthG}$ Ethanol production from glucose uptake</td>
<td>0.47 kg/kg</td>
</tr>
<tr>
<td>76</td>
<td>$Y_{CellG}$ Biomass growth on glucose</td>
<td>0.115 kg/kg</td>
</tr>
<tr>
<td>77</td>
<td>$m_{G}$ Maintenance coefficient for biomass growth on glucose</td>
<td>$2.6944 \times 10^{-5}$ 1/s</td>
</tr>
<tr>
<td>78</td>
<td>$q_{\text{Max}G}$ Maximum glucose uptake rate</td>
<td>0.000318 1/s</td>
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<tr>
<td>79</td>
<td>$K_{IPX}$ Xylose uptake self inhibition parameter</td>
<td>81.3 g/kg</td>
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<tr>
<td>80</td>
<td>$K_{ISP}$ Xylose uptake self inhibition parameter</td>
<td>3.4 g/kg</td>
</tr>
<tr>
<td>81</td>
<td>$P_{MPX}$ Ethanol inhibition on xylose uptake</td>
<td>100.2 g/kg</td>
</tr>
<tr>
<td>82</td>
<td>$\gamma_{X}$ Ethanol inhibition on xylose uptake</td>
<td>0.608 –</td>
</tr>
<tr>
<td>83</td>
<td>$Y_{EthX}$ Ethanol production from xylose uptake</td>
<td>0.4 kg/kg</td>
</tr>
<tr>
<td>84</td>
<td>$Y_{CellX}$ Biomass growth on xylose</td>
<td>0.162 kg/kg</td>
</tr>
<tr>
<td>85</td>
<td>$m_{X}$ Maintenance coefficient for biomass growth on xylose</td>
<td>$1.8611 \times 10^{-5}$ 1/s</td>
</tr>
<tr>
<td>86</td>
<td>$q_{\text{Max}X}$ Maximum xylose uptake rate</td>
<td>0.00083444 1/s</td>
</tr>
<tr>
<td>87</td>
<td>$K_{ACS}$ Acetate uptake self inhibition</td>
<td>2.5 g/kg</td>
</tr>
<tr>
<td>88</td>
<td>$K_{IAcG}$ Acetate inhibition on glucose uptake</td>
<td>2.74 g/kg</td>
</tr>
<tr>
<td>89</td>
<td>$K_{IAcX}$ Acetate inhibition on xylose uptake</td>
<td>0.2 g/kg</td>
</tr>
<tr>
<td>90</td>
<td>$Y_{AcHMFF}$ Acetate production from 5-HMF uptake</td>
<td>0.23392 kg/kg</td>
</tr>
<tr>
<td>91</td>
<td>$Y_{CO_2S}$ CO$_2$ production from 5-HMF uptake</td>
<td>0.1 kg/kg</td>
</tr>
</tbody>
</table>
4. Correlation Matrices for Latin Hypercube Sampling in Uncertainty Analysis

As explained in the manuscript, the correlation matrix for the sensitive parameters set is a block diagonal matrix assumed to have the following structure:

\[
R = \begin{pmatrix}
R_P & 0 & 0 \\
0 & R_L & 0 \\
0 & 0 & R_F
\end{pmatrix}
\]  

(64)

where \( R_P, R_L \) and \( R_F \) are full matrices, and represent the correlation of the pretreatment, liquefaction and fermentation parameters grouped by refinery step. The numerical values are shown next:

\[
R_P = \begin{bmatrix}
1.00 & -0.54 & -0.61 & 0.00 & -0.12 & -0.51 \\
-0.54 & 1.00 & 0.16 & 0.00 & 0.26 & 0.74 \\
-0.61 & 0.16 & 1.00 & 0.00 & 0.01 & 0.14 \\
0.00 & 0.00 & 0.00 & 1.00 & 0.00 & 0.00 \\
-0.12 & 0.26 & 0.01 & 0.00 & 1.00 & 0.17 \\
-0.51 & 0.74 & 0.14 & 0.00 & 0.17 & 1.00
\end{bmatrix}
\]  

(65)

\[
R_L = \begin{bmatrix}
1.00 & 0.00 & 0.00 & -1.00 \\
0.00 & 1.00 & 0.00 & 0.00 \\
0.00 & 0.00 & 1.00 & 0.00 \\
-1.00 & 0.00 & 0.00 & 1.00
\end{bmatrix}
\]  

(66)
The uncertainty analysis is based on Latin Hypercube Sampling with correlation control. The correlation matrices are presented for each refinery step, i.e. \( \mathbf{R}_P \), \( \mathbf{R}_L \) and \( \mathbf{R}_F \).

\[
\mathbf{R}_F = \begin{bmatrix}
1.00 & -0.25 & -0.69 & 0.59 & -0.11 & 0.01 & 0.43 & 0.48 & -0.15 & -0.44 & 0.20 & -0.23 \\
-0.25 & 1.00 & 0.05 & -0.02 & 0.19 & -0.13 & -0.63 & -0.17 & -0.28 & 0.04 & 0.12 & 0.26 \\
-0.69 & 0.05 & 1.00 & -0.42 & -0.09 & -0.05 & -0.27 & -0.52 & 0.30 & 0.64 & -0.04 & -0.00 \\
0.59 & -0.02 & -0.42 & 1.00 & -0.22 & -0.08 & 0.03 & 0.72 & -0.03 & -0.59 & 0.21 & -0.65 \\
-0.11 & 0.19 & -0.09 & -0.22 & 1.00 & 0.11 & -0.30 & -0.33 & -0.34 & -0.17 & -0.09 & 0.45 \\
0.01 & -0.13 & -0.05 & -0.08 & 0.11 & 1.00 & -0.11 & -0.12 & -0.51 & 0.08 & 0.15 & 0.20 \\
0.43 & -0.63 & -0.27 & 0.03 & -0.30 & -0.11 & 1.00 & 0.45 & 0.56 & -0.30 & 0.01 & -0.41 \\
0.48 & -0.17 & -0.52 & 0.72 & -0.33 & -0.12 & 0.45 & 1.00 & 0.39 & -0.80 & 0.06 & -0.73 \\
-0.15 & -0.28 & 0.30 & -0.03 & -0.34 & -0.51 & 0.56 & 0.39 & 1.00 & -0.21 & -0.17 & -0.63 \\
-0.44 & 0.04 & 0.64 & -0.59 & -0.17 & 0.08 & -0.30 & -0.80 & -0.21 & 1.00 & -0.00 & 0.41 \\
0.20 & 0.12 & -0.04 & 0.21 & -0.09 & 0.15 & 0.01 & 0.06 & -0.17 & -0.00 & 1.00 & -0.02 \\
-0.23 & 0.26 & -0.00 & -0.65 & 0.45 & 0.20 & -0.41 & -0.73 & -0.63 & 0.41 & -0.02 & 1.00
\end{bmatrix}
\]

(67)

5. Conclusions

This supplementary material contains the modeling library for simulating a second generation bioethanol plant. The library consists of dynamic models for biomass steam pretreatment, enzymatic hydrolysis and C5-C6 co-fermentation. The uncertainty analysis is based on Latin Hypercube Sampling with correlation control. The correlation matrices are presented for each refinery step, i.e. \( \mathbf{R}_P \), \( \mathbf{R}_L \) and \( \mathbf{R}_F \).

References


