BIOMASS HYDROTHERMAL FRACCTIONATION MODELLING FOR DIFFERENT REACTORS: KINETICS & MASS TRANSFER

High Pressure Processes Group

TUHH Thermische Verfahrenstechnik

ÁLVARO CABEZA SÁNCHEZ

6th International Congress on GREEN PROCESS ENGINEERING

3 - 6 June 2018 TOULOUSE France

OBJECTIVES

Modelling & simulation

- Biomass hydrothermal fractionation (packed bed)
- Kinetic modelling & validation
- 3 different reactors: 3 L, 6 L & 40 L
- 3 biomasses: holm oak, catalpa and wheat straw
- Focused on hemicellulose (T around 180 ºC)
- Improvement of a preliminary approach (0.1 L)



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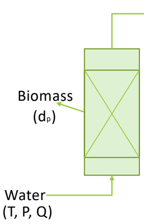
INITIAL MODEL

MECHANISM

- Oligomers & sugars
  - 1st soluble (high Mw)
  - Last (low Mw)
- pH variations
  - Deacetylation
  - H^+ consumption (buffering effect)
- Two phases
  - Mass transfer
  - Porosity changes
- Lignin as an inert



Assumptions:

- Isothermal
- No diffusion
- Globalised solid profiles

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INITIAL MODEL

MECHANISM

- Oligomers & sugars
  - 1st soluble (high Mw)
  - Last (low Mw)
- pH variations
  - Deacetylation
  - H^+ consumption (inert effect)
- Two phases
  - Mass transfer
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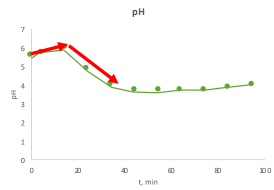

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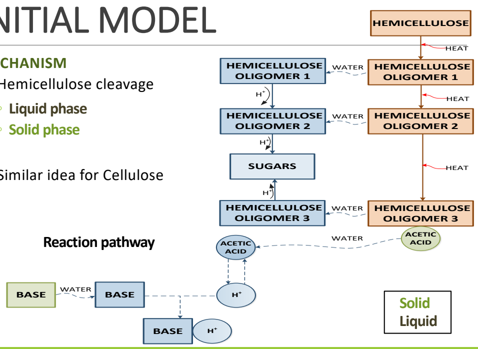
INITIAL MODEL

MECHANISM

- Hemicellulose cleavage
  - Liquid phase
  - Solid phase
- Similar idea for Cellulose



Reaction pathway

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INITIAL MODEL

MASS BALANCES

- Liquid (A)

$$\frac{\partial C_{A_j}}{\partial t} = \frac{1}{\varepsilon} \cdot \left[-\frac{u}{L} \cdot \frac{\partial C_{A_j}}{\partial z} - \varphi \cdot C_{A_j} \cdot \frac{dC_T}{dt} + k_j \cdot a \cdot \left(C_{A_j}^{*} - C_{A\ j}^{Av} \right) + r_j \right]$$

- Solid (B)

$$\frac{dC_{B_j}}{dt} = \frac{1}{1-\varepsilon} \cdot \left[r_j - \varphi \cdot C_{B_j} \cdot \frac{dC_T}{dt} - k_j \cdot a \cdot \left(C_{A_j}^{*} - C_{A\ j}^{Av} \right) \right]$$

$$\frac{d(1-\varepsilon) \cdot C_T}{dt} = \sum_{j=1}^{j=N} r_j - k_j \cdot a \cdot \left(C_{A_j}^{*} - C_{A\ j}^{Av} \right)$$ (inert mass balance)

TERMS

Time dependence
Convective flow
Extraction effect
Mass transfer
Reaction

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INITIAL MODEL

MASS BALANCES

- Extraction effect $\varphi \cdot C_{A/B_j} \cdot \frac{dC_T}{dt}$

$$\varepsilon = 1 - \varphi \cdot C_T \longrightarrow \varphi = f(biomass) \quad \varphi \neq f(t,z)$$

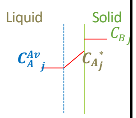
- Mass transfer $k_j \cdot a \cdot \left(C_{A_j}^* - C_{A\,j}^{Av}\right)$

$$C_{A_j}^* = H_j \cdot C_{B\,j}(t)$$

$$C_{A_j}^{Av} = \frac{1}{n} \cdot \sum_{z=0}^{Z=1} C_{A\,j}(z,t)$$

$$k_j \cdot a \cdot \left(C_{A_j}^* - C_{A\,j}^{Av}\right) \neq f(z)$$

$$k_j \cdot a \cdot \left(C_{A_j}^* - C_{A\,j}^{Av}\right) = f(t)$$



INITIAL MODEL

MASS BALANCES

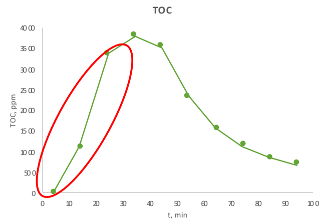
- Reaction → Autocatalytic kinetics

$$r_j = \sum_{i=1}^{i=n_{reac}} \theta_{i,j} \cdot r_i$$

$$r_i = k_i \cdot \prod_{j=1}^{j=n} C_j^{n_{i,j}} \cdot \left(1 - \alpha_{i,j} \cdot x_j\right)^{\beta_{i,j}}$$

$n_{i,j}=1$

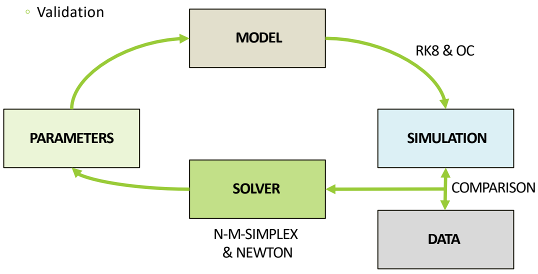
$n_{i,protons}\neq 1$



INITIAL MODEL

MASS BALANCES

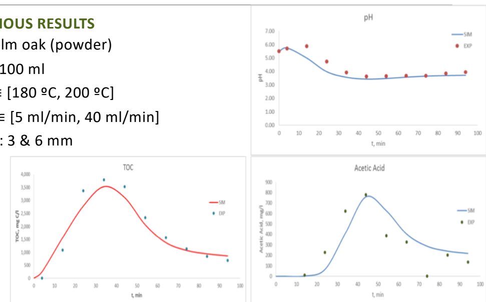
- Validation



INITIAL MODEL

PREVIOUS RESULTS

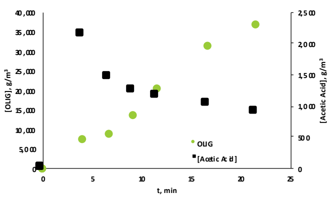
- Holm oak (powder)
- V: 100 ml
- T ∈ [180 ºC, 200 ºC]
- Q ∈ [5 ml/min, 40 ml/min]
- dp: 3 & 6 mm



MODIFIED MODEL

Model changes

- Issues
  - Acetic acid profile
  - Dissolved lignin profile
  - DP profile

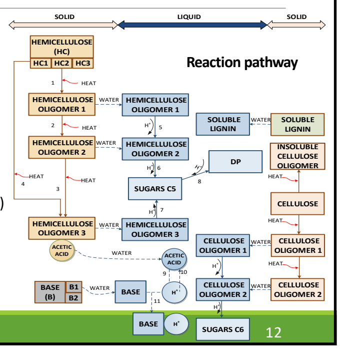


No Simultaneous extraction & deacetylation

MODIFIED MODEL

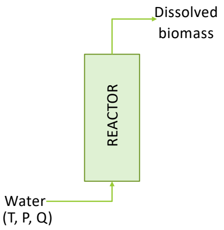
Model changes

- New mechanism
  - Sugar degradation
  - Soluble lignin
  - Direct deacetylation
- Three kinds of hemicellulose
  - Direct deacetylated (HC1)
  - "Easy" to extract (HC2)
  - Not able to be extracted (HC3)
- Two bases
  - Soluble (B1)
  - Insoluble (B2)
- Diffusive term in the LMB



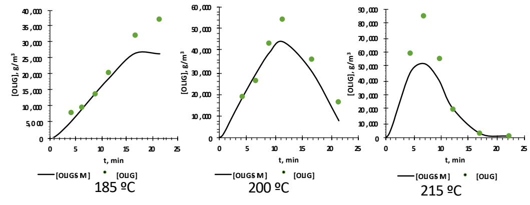
MODIFIED MODEL VALIDATION

Wheat straw (WS)
- Experimental
  - V: 3 L
  - T: 185, 200 & 215 ºC
  - Wheat straw (WS)
  - Q: 0.25 kg/min
  - M: 900 g (pellets)
- Reactor output
  - Sugar profile
  - Oligomer profile
  - pH profile
  - DP profile
  - Acetic acid profile
  - Dissolved lignin profile



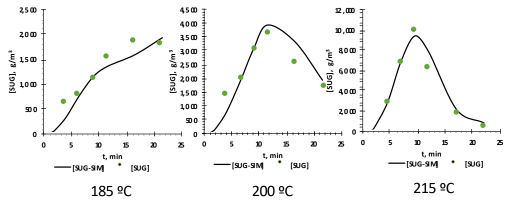
MODIFIED MODEL VALIDATION

Wheat straw (WS)
- Oligomers



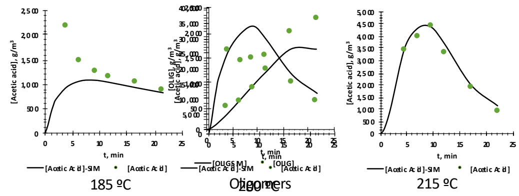
MODIFIED MODEL VALIDATION

Wheat straw (WS)
- Sugars



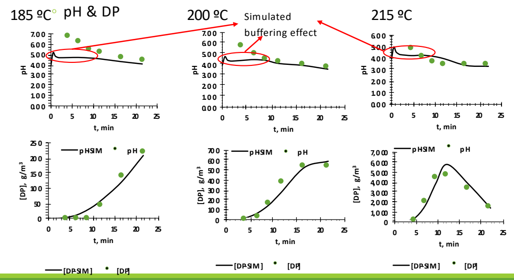
MODIFIED MODEL VALIDATION

Wheat straw (WS)
- Acetic Acid



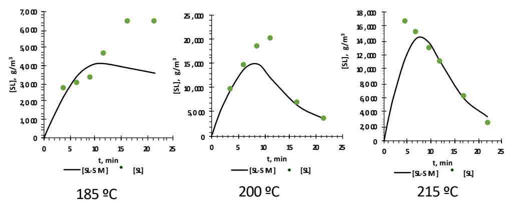
MODIFIED MODEL VALIDATION

Wheat straw (WS)
- pH & DP



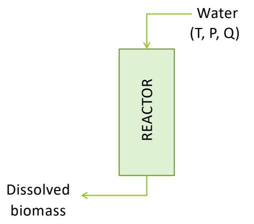
MODIFIED MODEL VALIDATION

Wheat straw (WS)
- Soluble lignin



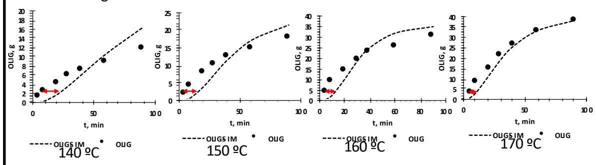
MODIFIED MODEL VALIDATION

Catalpa (CAT)
- Experimental
  - V: 6 L
  - T: 140, 150, 160 & 170 ºC
  - Catalpa (CAT)
  - Q: 0.25 kg/min
  - M: 600 g (powder)
- Reactor output
  - Sugar profile
  - Oligomer profile
  - Acetic acid profile
  - pH profile



MODIFIED MODEL VALIDATION

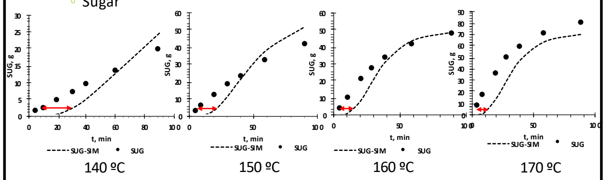
Catalpa (CAT)
- Oligomer



- Heating time
- Hemicellulose initially soluble (MW & Acetic Acid)

MODIFIED MODEL VALIDATION

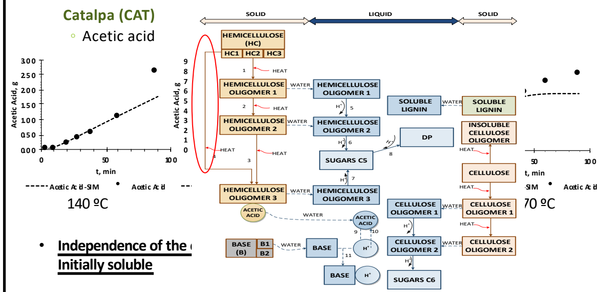
Catalpa (CAT)
- Sugar



- Heating time
- Hemicellulose initially soluble (MW & Acetic Acid)

MODIFIED MODEL VALIDATION

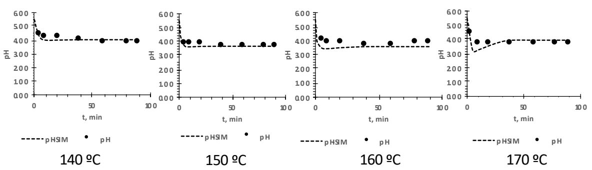
Catalpa (CAT)
- Acetic acid



- Independence of the Initially soluble

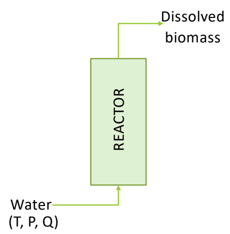
MODIFIED MODEL VALIDATION

Catalpa (CAT)
- pH



MODIFIED MODEL VALIDATION

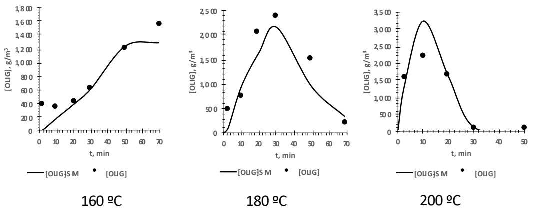
Holm Oak (HO40)
- Experimental
  - V: 40 L
  - T: 160, 180 & 200 ºC
  - Holm oak (HO40)
  - Q: 185 kg/min
  - M: 10 kg (splinters)
- Reactor output
  - Sugar profile
  - Oligomer profile
  - Acetic acid profile
  - pH profile
  - DP profile



MODIFIED MODEL VALIDATION

Holm Oak (HO40)

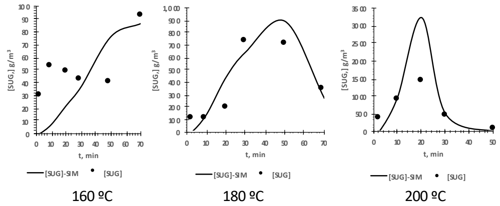
- Oligomer



MODIFIED MODEL VALIDATION

Holm Oak (HO40)

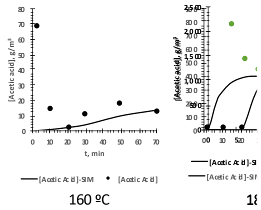
- Sugar

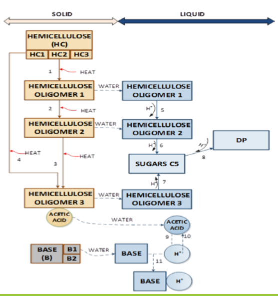


MODIFIED MODEL VALIDATION

Holm Oak (HO40)

- Acetic Acid

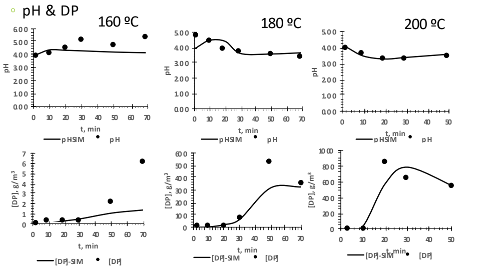




MODIFIED MODEL VALIDATION

Holm Oak (HO40)

- pH & DP



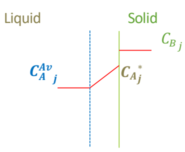
PARAMETERS ANALYSIS

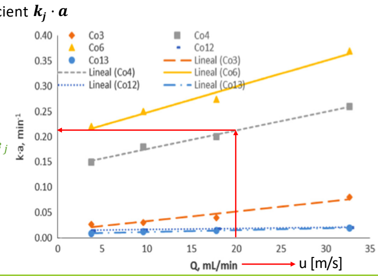
[1] A. Cabeza, F. Sobrón, F.M. Yedro, J. García-Serna, Two-phase modelling and simulation of the hydrothermal fractionation of holm oak in a packed bed reactor with hot pressurized water, Chemical Engineering Science, Volume 138, 2015, Pages 59-70, ISSN 0009-2509

Analysis of the parameters

- Mass transfer coefficient $k_j \cdot a$
  - From previous work[1]

$$k_j \cdot a = f(u)$$

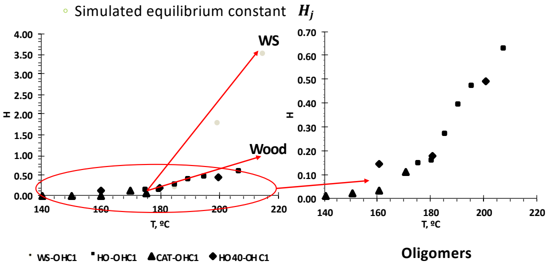




PARAMETERS ANALYSIS

Analysis of the parameters

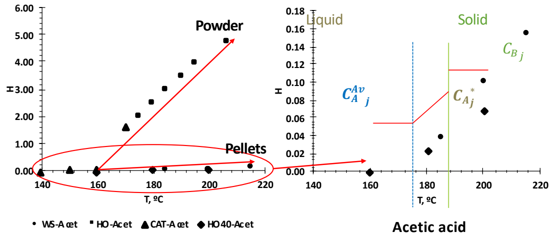
- Simulated equilibrium constant H_j



PARAMETERS ANALYSIS

Analysis of the parameters

- Simulated equilibrium constant H_j

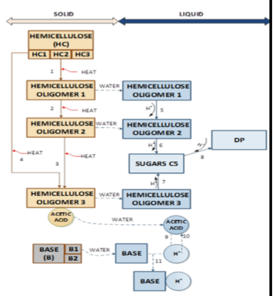


[2]Rissanen, J.V., Grénman, H., Willför, S., Murzin, D.Y., Salmi, T., 2014. Spruce Hemicellulose for Chemicals Using Aqueous Extraction: Kinetics, Mass Transfer, and Modeling. Industrial & Engineering Chemistry Research 53, 6341-6350

PARAMETERS ANALYSIS

Analysis of the parameters

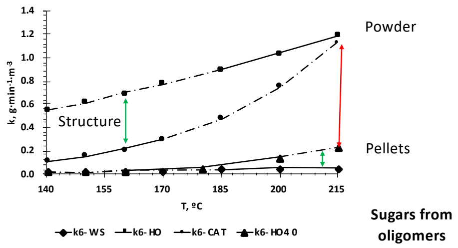
- Kinetics k_i
  - Kinetic rates similar
    - 1, 2 , 5, 9 and 10
  - Different kinetic rates
    - 3, 4, 6, 7, 8 and 11
    - Similar order of magnitude
    - Morphology (pellets vs powder)[2]
    - Structural reasons
      - Oligomers length
      - Acetyl content



PARAMETERS ANALYSIS

Analysis of the parameters

- Kinetics k_i

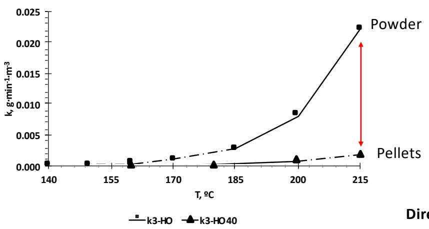


Sugars from oligomers

PARAMETERS ANALYSIS

Analysis of the parameters

- Kinetics k_i



Direct deacetylation

PARAMETERS ANALYSIS

Analysis of the parameters

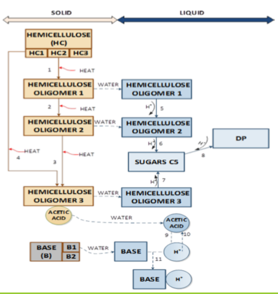
- Proton reaction order $n_{i,j}$
  - Reactions: 6, 7 and 8

$$K = e^{-\frac{Ea}{R\cdot T}+\ln(A)} = A\cdot e^{\frac{-Ea+f(H^+)}{R\cdot T}};$$

$$if\ f(H^+) = \ln(H^+);$$

$$K = A\cdot e^{\left(-\frac{Ea}{R\cdot T}\right)}\cdot e^{\ln(H^+)^{1/RT}} = A\cdot H^{+1/RT}\cdot e^{-\frac{Ea}{R\cdot T}}$$

$n_{i,j}$



PARAMETERS ANALYSIS

Analysis of the parameters

- Other parameters
  - Autocatalytic coefficients → Function of the temperature
  - Liquid effective diffusivity (axial) → Function of the temperature
  - Acetic acid stoichiometric coefficient → 0.18-0.30 g/g HC
  - HC1(40%) & HC2 (60%) values
  - B1 (10%) and B2 (90%) values
- Other simulated data
  - Bed porosity
  - Internal profiles: liquid and solid
  - Global mas balance error: 4-6 %

CONCLUSIONS

Conclusions

- Kinetic model validated
  - 3 different tubular reactors used (3.0 L, 6.0 L and 40.0 L)
  - 3 different biomass tested (HO, WS & CAT)

  Errors between 8-38 %
- Main sources of errors
  - Initial heating
  - Lab scale assumptions (like isothermal reactor)
  - pH simulation (reactions: 3, 4, 6, 7, 8 and 11)

Further work

- Energy balance
- Initial heating period
- Buffering effect

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ACKNOWLEDGMENTS

Thermal separation processes institute (Technical university of Hamburg)

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- Internship program for FPU grants 2016 (ref EST16/00186)

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TUHH Thermische Verfahrenstechnik

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