Universidad de Valladolid

2nd International Conference on Green Chemistry and Sustainable Engineering

MODELLING OF A LIGNOCELLULOSIC BIOMASS FRACTIONATION PROCESS IN A LAB-SCALE BIOREFINERY WITH HOT PRESSURIZED WATER

shyman
Sustainable Hydrothermal Manufacturing of Nanomaterials
Large-scale green & economical synthesis of nanoparticles and nanostructures

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FPU2013/01516
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OBJECTIVES

Biomass fractionation modelling

- Set of physical phenomena
- Molecular weight
- Auto-hydrolysis
- Deacetylation

Reactor inside simulation

- Solid phase
- Liquid phase
- Oligomer cleaving

EXPERIMENTAL

Extraction column

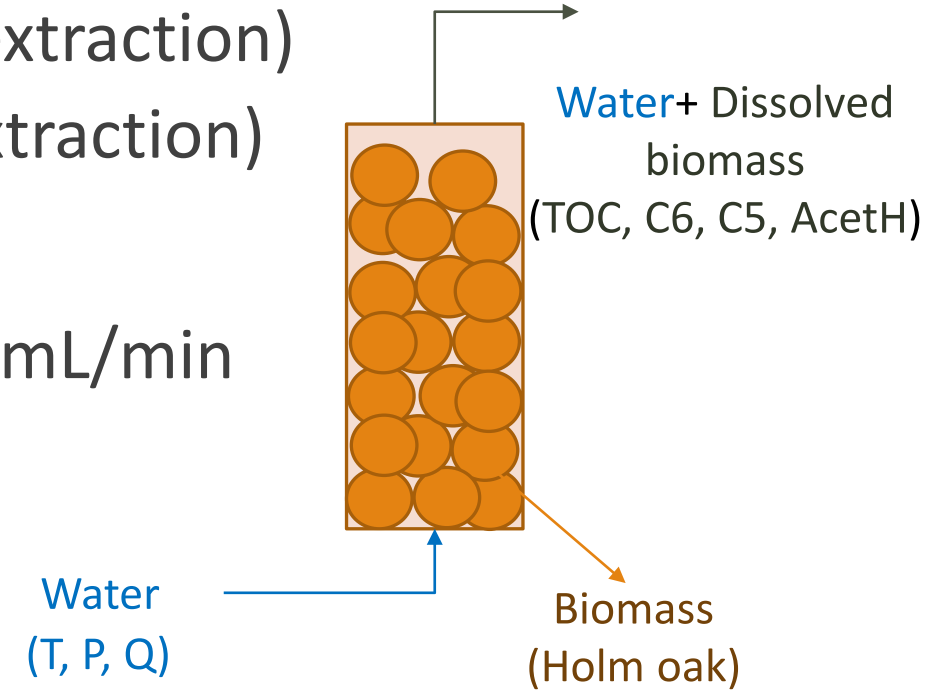
Isothermal conditions (temperature ranges)

- 1st : 140 ºC-180 ºC (HC extraction)
- 2nd : 240 ºC-260 ºC (C extraction)

4 flow rates

- 6.5, 11.0, 15.0 and 28.0 mL/min

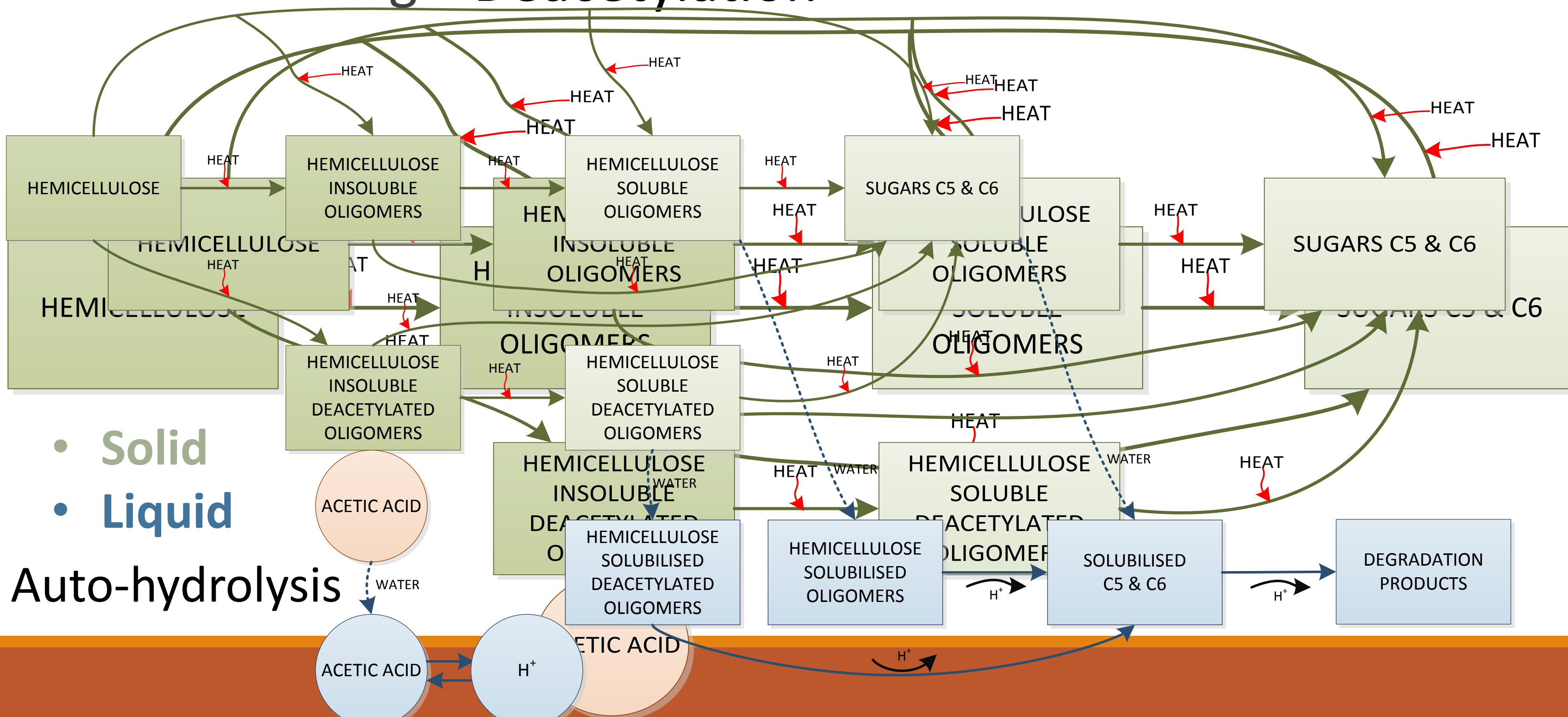
8 Experiments



MODELLING: Reaction pathway

Hemicellulose

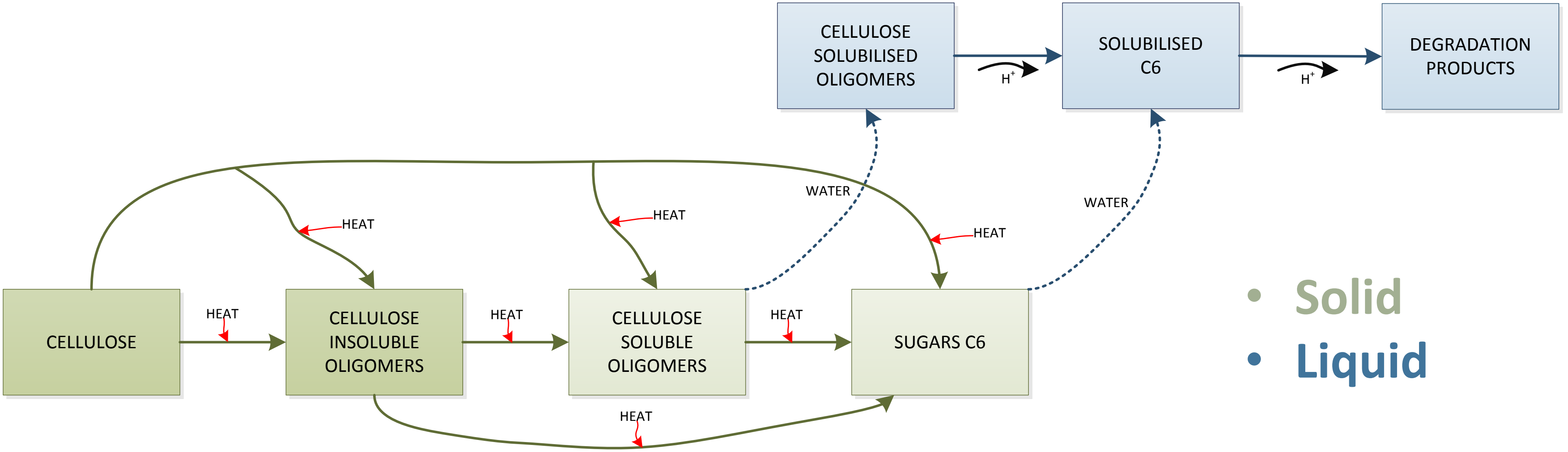
- Cleaving + Deacetylation + Solubilisation



MODELLING: Reaction pathway

Cellulose

- Cleaving + Solubilisation+ Auto-hydrolysis



- Solid
- Liquid

MODELLING: Reaction pathway

Lignin

- As an inert

Structural effects

- 2 Hemicellulose & Cellulose
  - Easy to extract
  - Difficult to extract

Oligomer cleaving

- 60 members population

245 compounds

MODELLING: Kinetics

Solid phase

- Based on an Auto catalytic expression

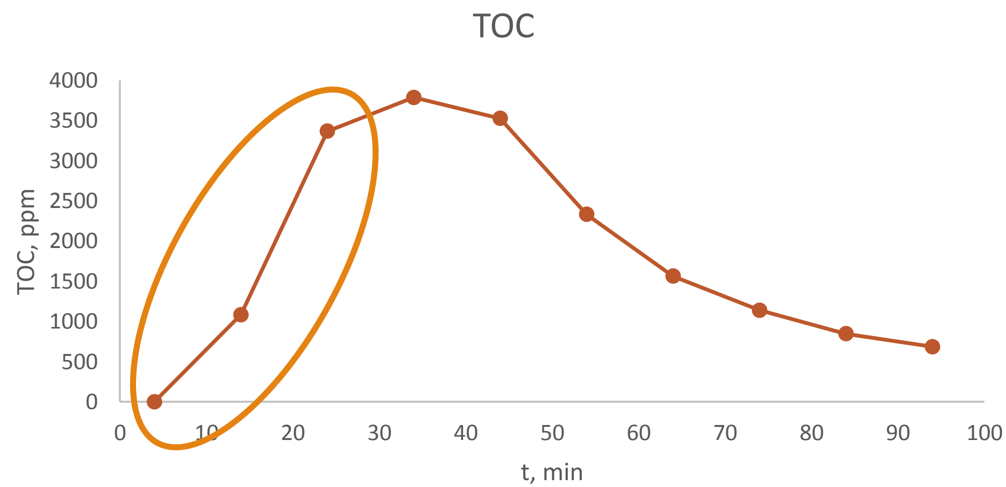
$$r_j = -k_{d_j} \cdot C_{S_j} \cdot F_{auto} \cdot \sum_{i=1}^{N} \alpha_{i,j} + \sum_{i=1}^{N} \alpha_{j,i} \cdot F_{auto} \cdot k_{d_i} \cdot C_{S_i}$$

All the compounds produced by "j"

All the compounds that produce "j"

$$F_{auto} = \left(1 - 0.99 \cdot f\left(m_j, m_T^{-1}\right)\right)^{\beta_{i,j}}$$

$$\alpha_{i,j} = f\left(MW_i, MW_j\right)$$



MODELLING: Kinetics

Liquid phase

- Similar to solid phase

$$r_j = -k_{L_j} \cdot C_{L_j} \cdot C_{H^+}^{n_1} \cdot \sum_{i=1}^{N} \alpha_{i,j} + \sum_{i=1}^{N} \alpha_{j,i} \cdot C_{H^+}^{n_1} \cdot k_{L_i} \cdot C_{L_i}$$

- Auto-hydrolysis: proton order as a temperature

function

$$K = e^{A - \frac{(E_1 + f(C_{H^+}))}{R \cdot T}} = e^{A} \cdot e^{-\frac{(E_1)}{R \cdot T}} \cdot e^{-\frac{f(C_{H^+})}{RT}}$$

$$f(C_{H^+}) = \ln(C_{H^+})$$

$$K = e^{A} \cdot e^{-\frac{(E_1)}{R \cdot T}} \cdot C_{H^+}^{-\frac{1}{R \cdot T}}$$

$$n_1 = -\frac{1}{RT} \longrightarrow n_1 = f(T)$$

MODELLING: Mass balances

Liquid phase

$$\frac{\partial C_{L_j}}{\partial t} = \frac{1}{\mathcal{E}} \cdot \left[r_j - \frac{u}{L} \cdot \frac{\partial C_{L_j}}{\partial z} - \varphi \cdot C_{L_j} \cdot \frac{\partial C_t}{\partial t} + k_j \cdot a \cdot \left(C_{L_j}^{*} - C_{L_j} \right) \right]$$

Accumulation = reaction + convection + porosity changes effects + mass transfer

Solid phase

$$\frac{\partial C_{S_j}}{\partial t} = \frac{1}{1-\mathcal{E}} \cdot \left[r_j - \varphi \cdot C_{S_j} \cdot \frac{\partial C_t}{\partial t} - k_j \cdot a \cdot \left(C_{L_j}^{*} - C_{L_j} \right) \right]$$

$$\frac{\partial (1-\mathcal{E}) \cdot \left(C_t - \sum_{j=1}^{j=N} C_{S_j} \right)}{\partial t} = 0$$

Inert mass balance

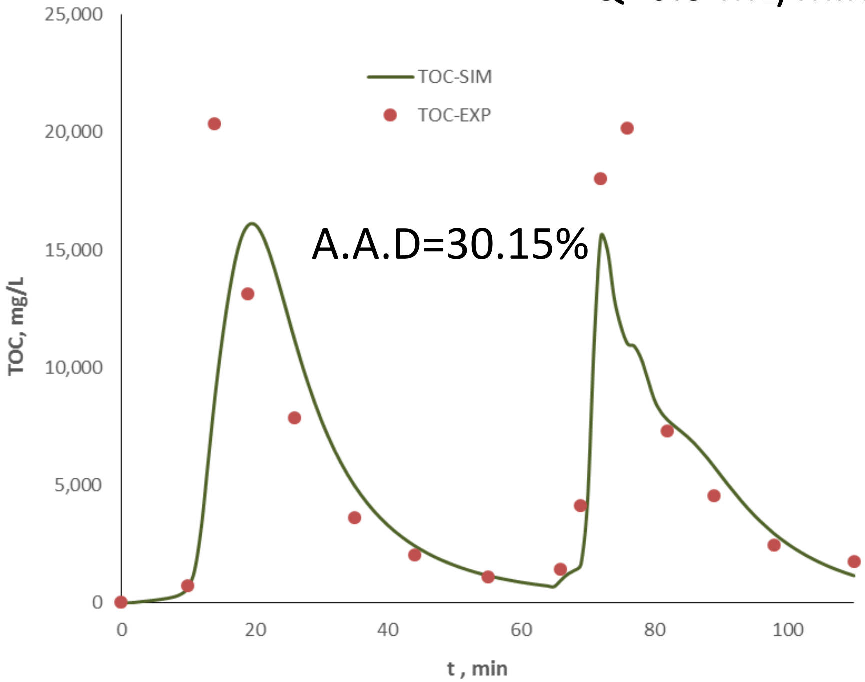
$$\mathcal{E} = 1 - \varphi \cdot C_t$$

Porosity as function of solid concentration

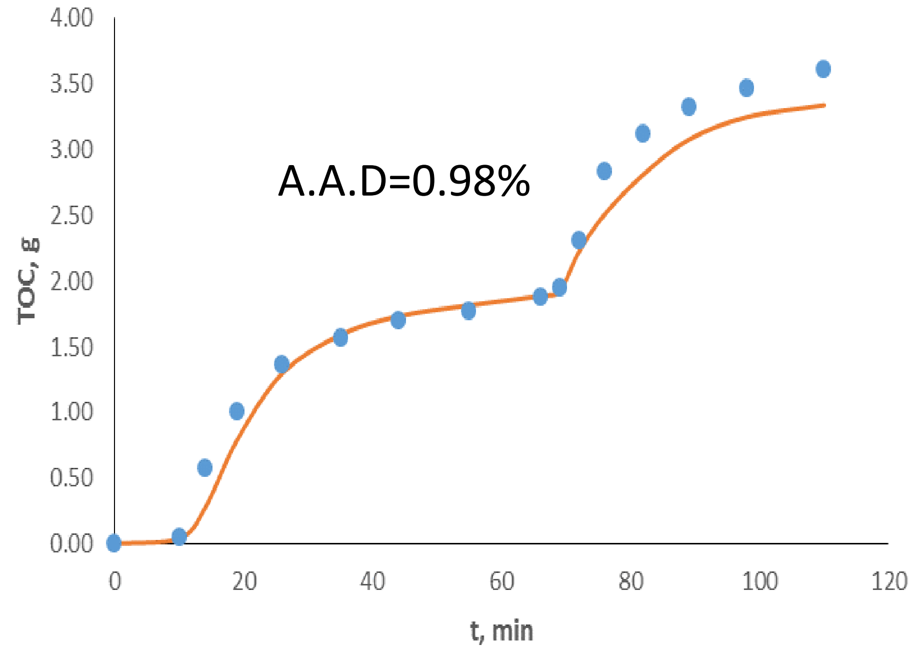
RESULTS: Fittings

TOC

Q=6.5 mL/min & T=180-260 ºC

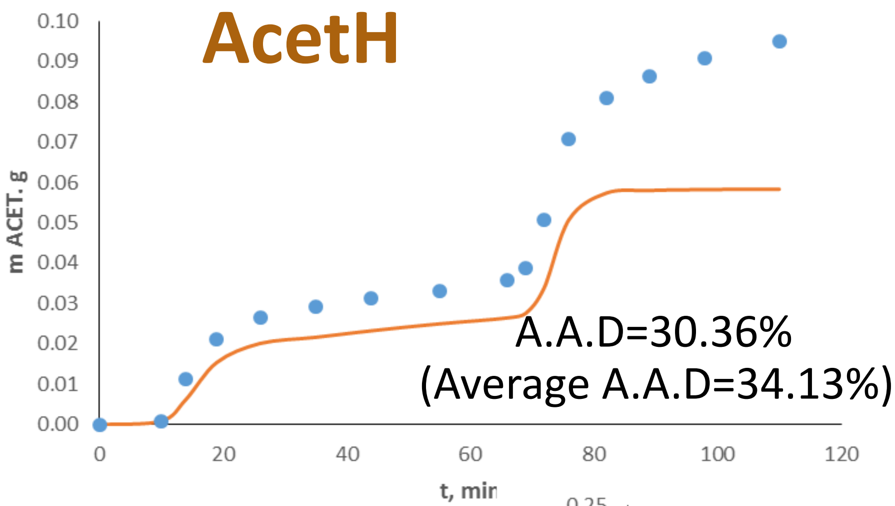


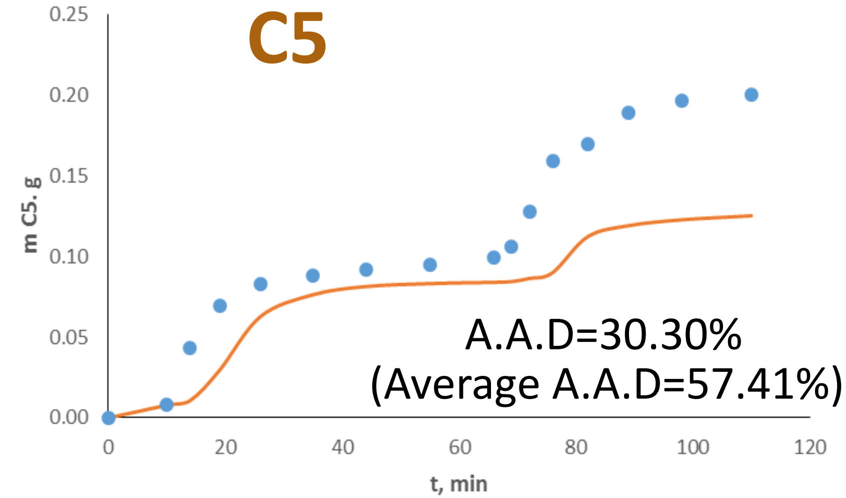
(Average A.A.D=42.62%)

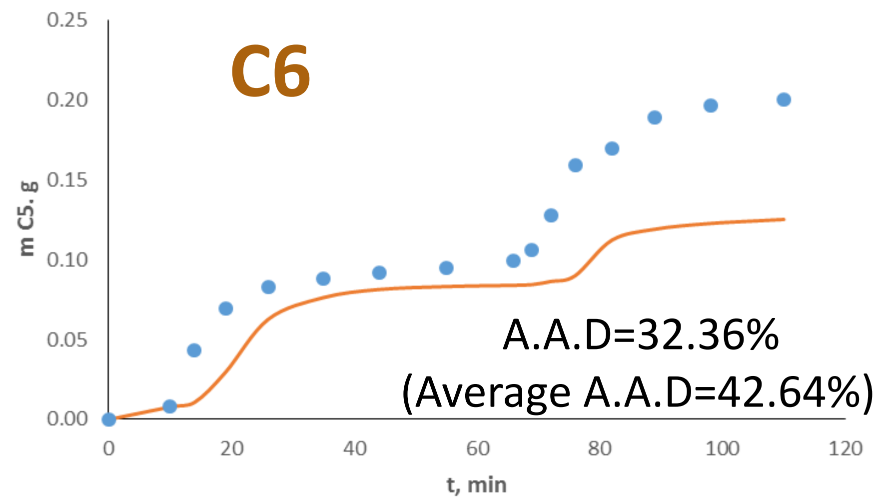


(Average A.A.D=19.06%)

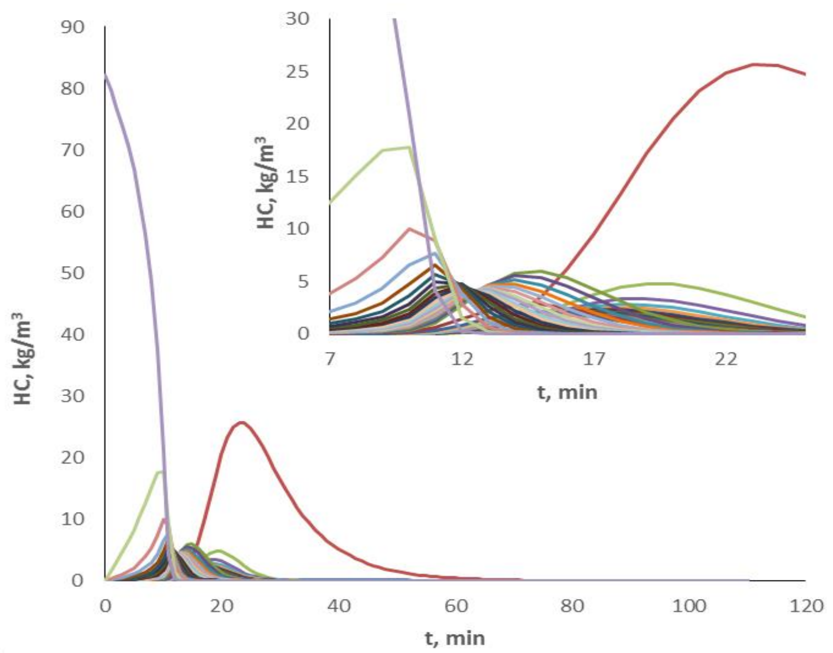
RESULTS: Product simulation



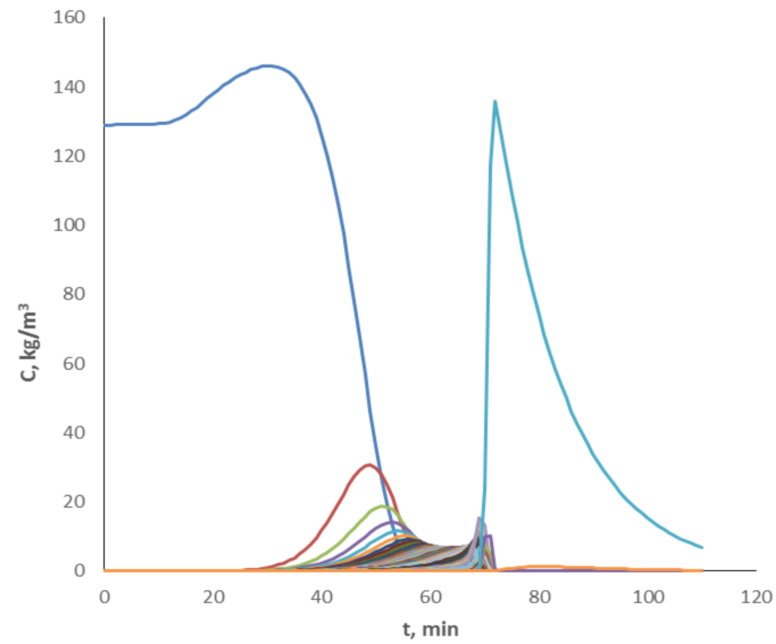




RESULTS: Solid cleaving simulation



Hemicellulose



Cellulose

CONCLUSIONS

Modelling for biomass fractionation

- Subcritical range (140 ºC – 260 ºC)
- Flow & temperature effect
- Set of physical phenomena
- MW effect
- Low TOC deviation **(<20%)**
- *<u>General for lignocellulosic biomass</u>*

Simulation

- *<u>Oligomer cleaving</u>*
- Reactor behaviour

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AAD considerations

Reasons

- TOC vs HPLC data → discrepancy around 20%
- Dilution → fluctuating profiles
- Sample biodiversity → different behaviour at the same conditions

Solution

- Focusing the analysis on HPLC data
  - Optimal conditions for hemicelluloses extraction from Eucalyptus globulus wood: hydrothermal treatment in a semi-continuous reactor, Fuel Processing Technology 148 (2016) 350–360

AAD considerations