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# MODELLING AND SIMULATION OF A HOLM OAK FRACTIONATION PROCESS IN A PACKED BED WITH HOT PRESSURIZED...

Conference Paper · June 2015

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## 1 INTRODUCTION AND OBJECTIVES

The production of fuels from biomass has been considered as a sustainable solution to the energetic problem related with the depletion of the petroleum sources. This idea have been studied extensively and it has been proved that the biomass sugar fraction can be recovered and transformed into liquid combustibles by several ways, such as **hydrothermal hydrolysis**. This type of hydrolysis would be one of the most promising option due to the fact that it only needs water to break biomass. However, a **kinetic model** which could reproduce the experimental behaviour taking into account the observed physical phenomena in a continuous system (like porosity variations) has not been fully developed.

### Objectives

- **Hydrothermal degradation modelling.**
  - How the fractionation takes place.
  - Autohydrolysis. Role of the pH.
  - Mass transfer effect. Solid mass variation effect.
  - Subcritical water.
  - Model **validation**.
- **Behaviour prediction.**
  - pH.
  - Sugars.
  - TOC.

## NOMENCLATURE

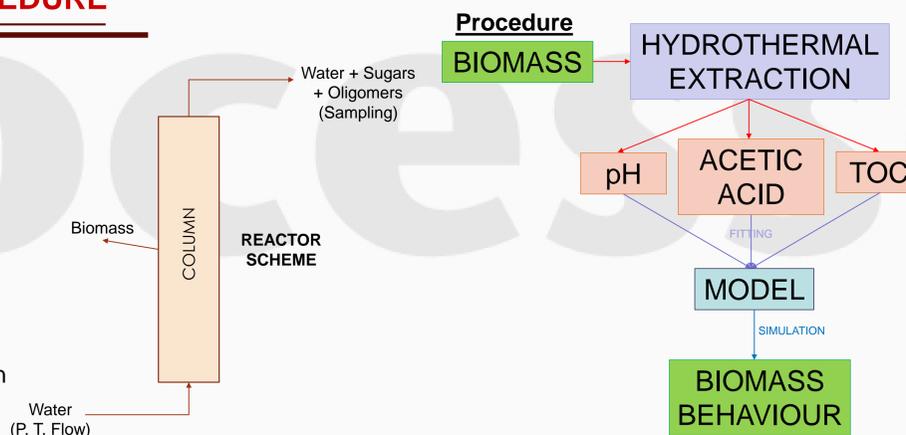
### Hydrothermal fractionation

$\epsilon$ : Porosity of the bed.  
 $j$ : Number of the compound.  
 $i$ : Number of the reaction.  
 $C_{Bj}$ : Concentration of "j" in the solid.  
 $r_j$ : reaction of "j".  
 $C_{Aj}$ : equilibrium concentration of "j".  
 $C_{Aj}$ : Concentration of "j" in the liquid.  
 $C_T$ : total solid concentration.  
 $\varphi$ : Relation factor between the porosity and the total solid concentration.  
 $u$ : liquid velocity.  
 $L$ : reactor length.  
 $Z$ : coordinate along the reactor.  
 $t$ : operating time  
 $k_a$ : mass transfer coefficient.  
 $r_i$ : Reaction number "i".  
 $\theta_{ij}$ : Stoichiometric coefficient of "j" in the reaction "i".  
 $n_{\text{reac}}$ : Total number of reactions.  
 $n_c$ : Total number of compounds.  
 $k_i$ : Kinetic constant of the reaction "i" (Arrhenius' type).  
 $C_j$ : Concentration of "j".  
 $n_{ij}$ : Reaction order of "j" in the reaction "i".  
 $\alpha_{ij}, \beta_{ij}$ : Autocatalytic coefficients of "j" in reaction "i".  
 $x_j$ : Instant mass fraction of "j".

## 2 EXPERIMENTAL SET-UP AND PROCEDURE

### Operating conditions and experimental set-up

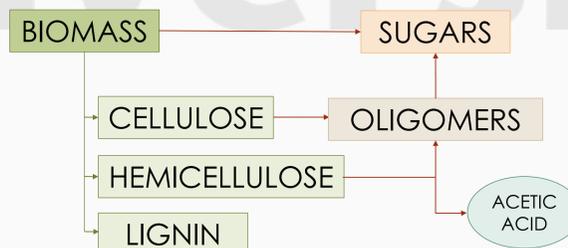
- Device: Stainless steel tubular reactor.
- Length: 38 cm.
- O.D.: ½ inch.
- Subcritical water.
- P= 100 bar.
- $T_\epsilon$  (175 °C, 204 °C)
- Volumetric flowe (5 ml/min, 40 ml/min),
- Biomass sample: 5 g (holm oak).
- Particle diameter: 3 and 6 mm.
- pH, TOC and acetic acid concentration monitoring.
- Operating time: 94 min.



## 3 MODEL AND REACTION PATHWAY

### Reaction pathway.

- Oligomer formation.
  - First soluble oligomer.
  - Last oligomer before sugar formation (dimer).
- pH variations.
  - Deacetylation reactions.
  - Autohydrolysis.
- Two phases.
  - Porosity variations.
  - Mass transfer between solid and liquid.
- Lignin as an inert.
  - Soluble lignin < 2.36wt%.
- Mild temperatures  $\Rightarrow$  Low production of degradation products.



### Model.

- Partial mass balances.
- Solid phase.

$$\frac{dC_{Bj}}{dt} = \frac{1}{1-\epsilon} \left[ r_j - \varphi \cdot C_{Bj} \cdot \frac{dC_T}{dt} - k_j \cdot a \cdot (C_{Aj}^* - C_{Aj}) \right]$$

$$\frac{\delta C_{Aj}}{\delta t} = \frac{1}{\epsilon} \left[ \frac{D_j}{L^2} \cdot \frac{\delta^2 C_{Aj}}{\delta x^2} - \frac{u}{L} \cdot \frac{\delta C_{Aj}}{\delta x} - \varphi \cdot C_{Aj} \cdot \frac{dC_T}{dt} + k_j \cdot a \cdot (C_{Aj}^* - C_{Aj}) + r_j \right]$$

- Kinetics.

$$r_j = \sum_{i=1}^{i=n_{\text{reac}}} \theta_{i,j} \cdot r_i \begin{cases} r_i = k_i \cdot \prod_{j=1}^{j=n_i} C_j^{n_{i,j}} \cdot (1 - \alpha_{i,j} \cdot x_j)^{\beta_{i,j}} & \text{(Solid phase)} \\ r_i = k_i \cdot C_{\text{prot}} \cdot \prod_{j=1}^{j=n_i} C_j^{n_{i,j}} \cdot (1 - \alpha_{i,j} \cdot x_j)^{\beta_{i,j}} & \text{(Liquid phase)} \end{cases}$$

## 4 RESULTS AND DISCUSSION

- **TOC, pH and acetic acid** concentration were adjusted with **A.A.D.** (Absolute average Deviation) of **16,3%, 6,6% and 44,4%** respectively (Figure 1-3)\*.
- The **final mass** in the **solid (A.A.D = 8.2%)** and the global behaviour of the system were simulated.
- **Hemicellulose simulation agrees** with the experimental data reported by **others authors** (extraction around 80% at 170°C and as oligomers).
- Cellulose simulation showed some discrepancies with previous studies. These discrepancies could be caused due to the fact that the pH was lower during the operation and because our system is a semi continuous process (mass transfer improvement).

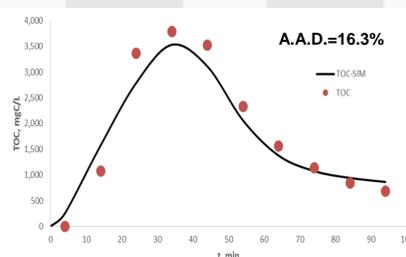


Figure 1: TOC fitting.

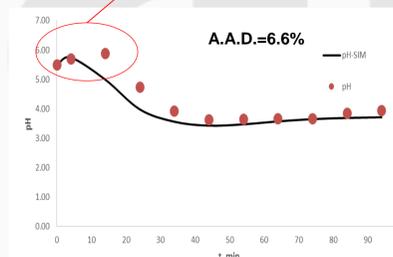


Figure 3: pH fitting.

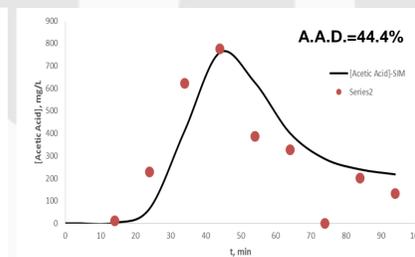


Figure 2: Acetic acid fitting.

This increment in the pH could be caused by some basic compound which would be present in biomass (like inert ashes.)

\*Fittings done for the experiment at 175 °C, 3 mm of particle diameter and a volumetric flow of 5 ml/min.

## 5 CONCLUSIONS

- A kinetic model for holm oak hydrothermal degradation in a packed bed reactor was done (deviations: TOC 16.3%, pH 6.6% and acetic acid 44.4%).

- The model takes into account the main physical phenomena involved during the process (porosity & pH variations, solid solubility and sugar formation).
- The mass transfers between the solid and the liquid was also checked and the deviation was 8.2%.
- The simulation agrees with other author for hemicellulose but it presents some deviations in cellulose due to pH and mass transfer.