Kinetic model of condensable co-products release during biomass torrefaction

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What is biomass torrefaction?

- Smooth thermal decomposition in default of air
  - ➡ Between drying and pyrolysis
  - T = 200-300°C
  - Solid residence time = 10 min to several hours
  - Atmospheric pressure

Biomass $C_6H_9O_4$ + moisture~20%

Volatile matter:
- **Gas (CO, CO_2)**
- **Condensable species (H_2O, acids…)**

>70w%

Torrefied biomass $C_6H_8O_3$ +moisture~3%

Properties get more coal-like
- H/C and O/C decrease
- Hydrophobic nature
- Energy densification
- Better grindability and flowability

What is biomass torrefaction?

➡ **Biorefinery approach**

Burnt or removed as waste

↳ Source of **Green chemicals**

Biomass $C_6H_9O_4$ + moisture~20%

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- **Condensable species (H_2O, acids…)**

>70w%

Torrefied biomass $C_6H_8O_3$ +moisture~3%

Energy carrier

↳ Fuel suitable for { gasification / combustion

Objective and working plan

Objective:

To develop a model of biomass torrefaction able to predict both solid and volatile matter versus operating conditions and biomass composition.

Approach: summative contribution of the main biomass constituents

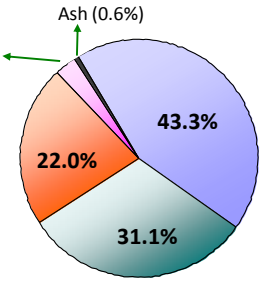
$$\Delta m_{biomass} = \Delta m_{cellulose} \cdot \%_{cellulose} + \Delta m_{lignin} \cdot \%_{lignin} + \Delta m_{hemicellulose} \cdot \%_{hemicellulose}$$

Working plan:

- Lab-scale experiments:
  - Thermogravimetric analysis
  - Torrefaction unit TORNADE
- Kinetic modelling

Biomass: beech

- Drying at 105°C
- Milling <200 µm

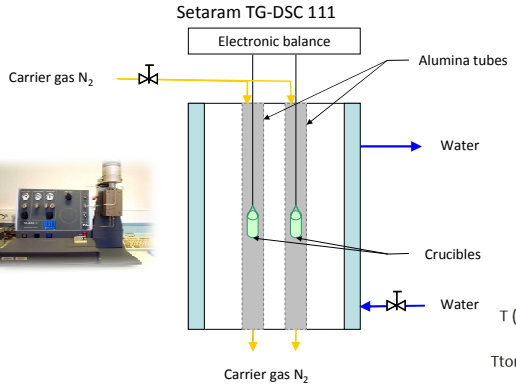


Lignin
Extracted from beech

Cellulose
Avicel

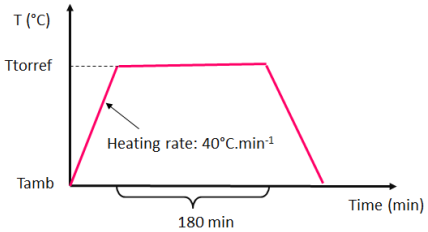
Xylan
Extracted from beech
(Representative of hemicellulose)

TGA: solid mass loss kinetics



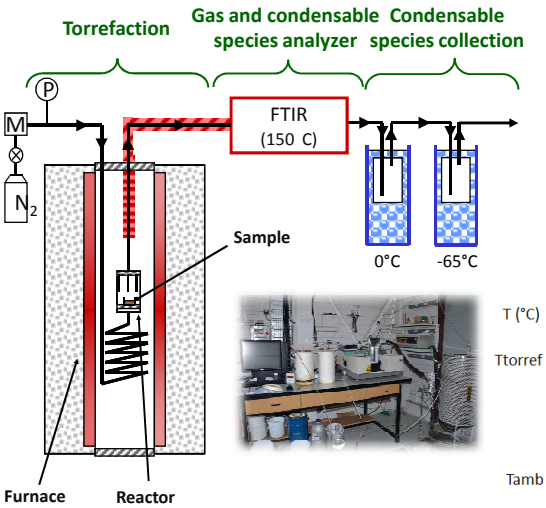
Study in chemical regime

Error between replicates<1%



Temperature	220;250;280;300°C
Gas atmosphere	N_2
Gas flowrate	30 mL.min^{-1}
Sample mass	4 mg

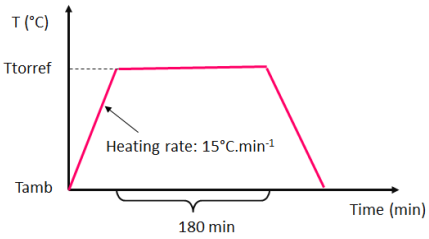
TORNADE: volatile matter production



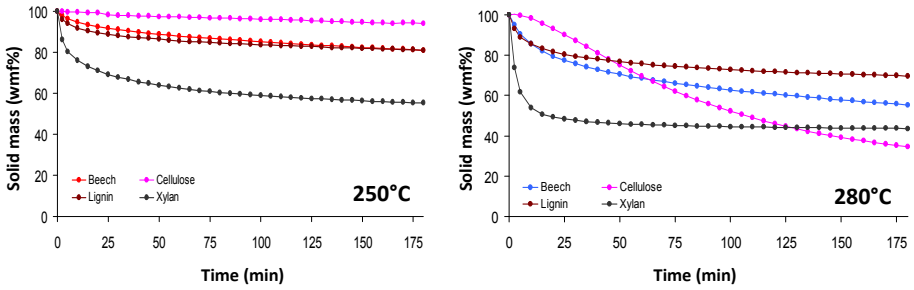
Study in chemical regime

Mass balance : 99 - 104%

Temperature	220;250;280;300°C
Gas atmosphere	N_2
Gas flowrate	1 NL.min^{-1}
Sample mass	100-200 mg

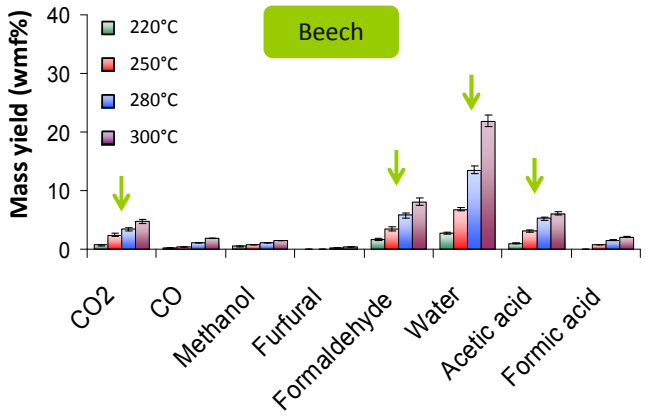


Kinetics of solid mass loss



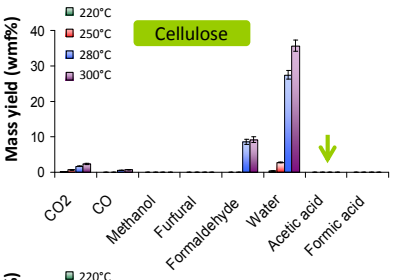
- **Lignin:** smooth and continuous mass loss
- **Xylan:** fast and (very) sharp mass loss
- **Cellulose:**
  - T ≤ 250°C: nearly no mass loss
  - T ≥ 280°C: slow mass loss then the highest rate

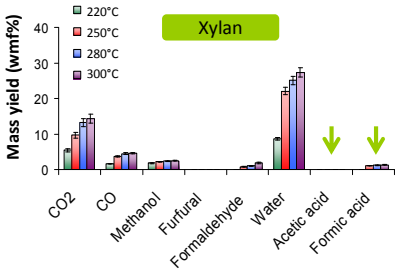
Gas and condensable species yields

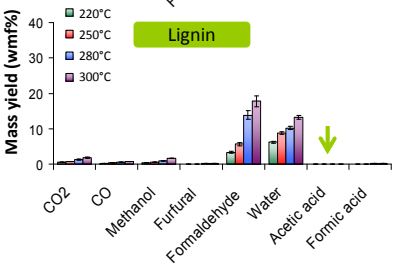


- Main species: **H_2O, formaldehyde, acetic acid, CO_2**
- Other species: CO, formic acid, methanol, furfural

Gas and condensable species yields

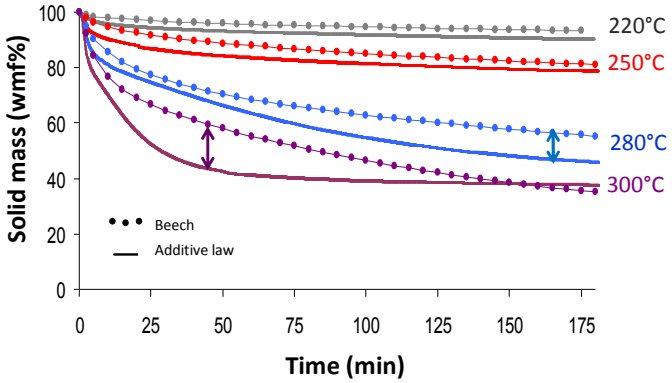






- Each species not produced by all constituents
  - ↳ Formic acid only produced by xylan torrefaction
- Acetic acid not produced by cellulose/lignin/xylan
  - ➡ Comes from acetyl groups of hemicellulose
    - ↳ Removed during extraction of xylan

Description with additive law?

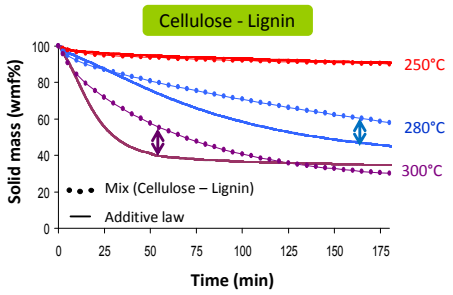


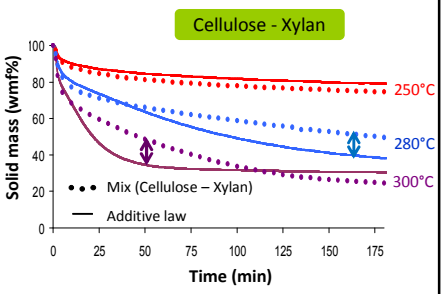
Correct at T ≤ 250°C

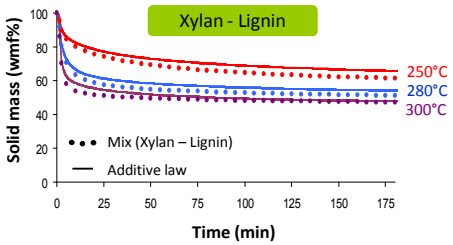
Not correct at T ≥ 280°C

→ **Interactions** between beech constituents from 280°C?

Mix of beech constituents





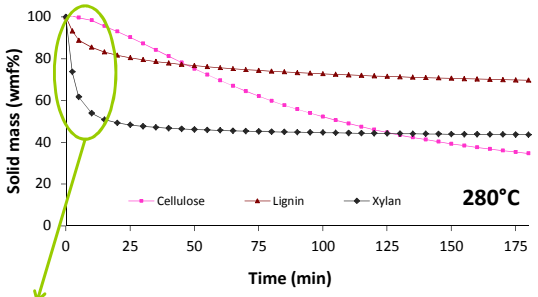


Interactions from 280°C between:

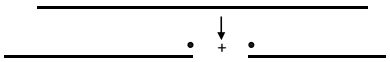
- Cellulose and Lignin
- Cellulose and Xylan

→
- Discrepancies linked with **cellulose decomposition**
- **Decrease** of the mix reaction **rate**

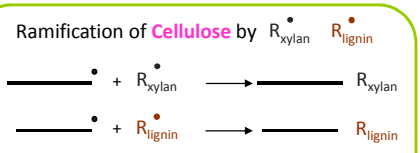
Interactions origin? One hypothesis



- Degradation of **Xylan** and **Lignin**:
  Production of numerous radicals $R^{\bullet}_{xylan}$ $R^{\bullet}_{lignin}$
  and/then of volatile matter
- Depolymerization of **Cellulose**



- Ramification of **Cellulose** by $R^{\bullet}_{xylan}$ $R^{\bullet}_{lignin}$



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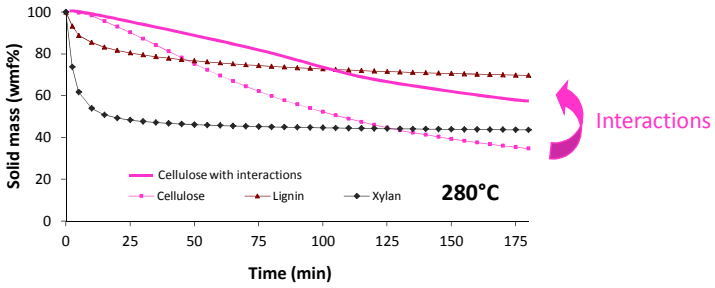

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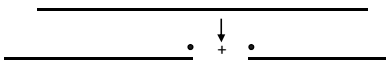

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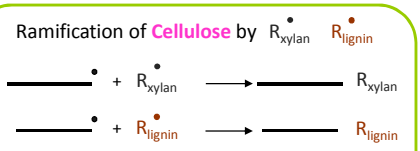
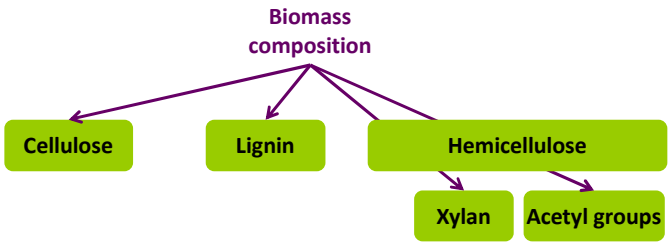


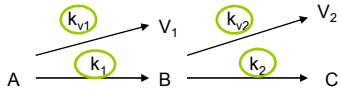
- Decrease of **Cellulose** decomposition rate

Kinetic model of biomass torrefaction



Constituents sub-models

- Model of Di Blasi (1997)
  - 2 steps
  - 2 parallel reactions
  - First-order kinetics
  - Arrhenius law



$$k_{ij} = A_i \exp\left(\frac{-Ea_i}{RT}\right)$$

- Yield of volatile species

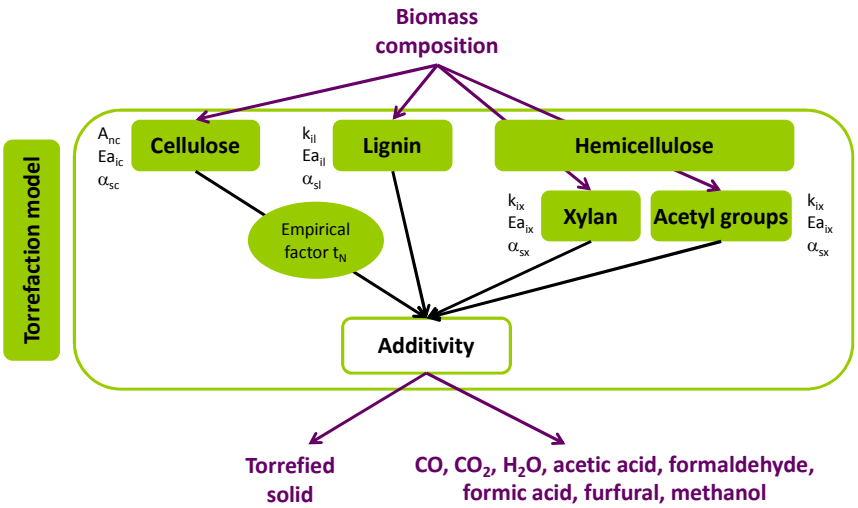
$$Y_{sj} = \alpha_{s1j} R_{V1} + \alpha_{s2j} R_{V2} \qquad \alpha_{s1j} = \alpha_{s2j}$$

Cellulose	H_2O, CO_2, CO, formaldehyde, furfural
Lignin	H_2O, CO_2, CO, formaldehyde, furfural, methanol
Xylan	H_2O, CO_2, CO, formaldehyde, methanol, formic acid
Acetyl groups	Acetic acid

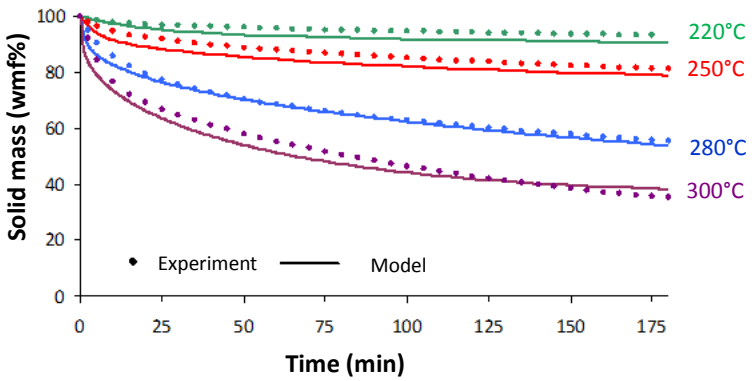
- Determination of the parameters
  - Least-squares minimization method

Di Blasi C, Lanzetta M (1997) Journal of Analytical and Applied Pyrolysis, 40-41:287.

Kinetic model of biomass torrefaction



Model validation



- Satisfactory results:
  - Prediction of solid yield with a difference < 3%
  - Estimation of 8 volatile species yields with differences < 40%

Conclusion

How to model torrefaction vs T, residence time and biomass composition ?

- **Sum of the main biomass constituents:**
  - Correct when T ≤ 250°C
  - Interactions between cellulose and other compounds when T ≥ 280°C
    - ↳ Empirical factor on cellulose decomposition rate
- Satisfactory prediction of:
  - Solid mass loss
  - The 8 main volatile species yields: **H_2O, formaldehyde, acetic acid, CO_2**, CO, formic acid, methanol, furfural
    - ↳ Not produced by all constituents

What's next?

- Confirm the **interactions origin**

- Apply the model to **other biomasses**

- Extend the model to **other volatile species** of interest for chemical industry

If you have any questions or want more details, please contact:

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