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# Study of self-heating phenomenon of torrefied wood in contact with oxygen

PhD. thesis started octobre 1<sup>st</sup> 2014

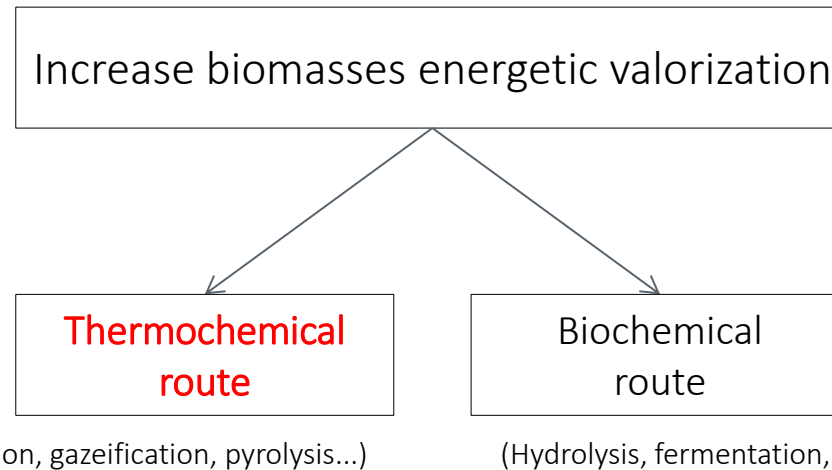


Brieuc Evangelista



## ■ How to achieve the energetic transition ?

### ➤ From fossil to renewable energy sources



### Weak fuel properties

- High water content
- Low energy density
- Poor grindability
- Poor decay resistancy



### Pretreatments

- Grinding
- AFEX
- **Torrefaction**
- ...



### Higher grade fuel

- Lower water content
- Higher energy density
- Better grindability
- Better decay resistancy

- Development of large scale torrefaction market expected to the decade to come (Thrän et al. 2016)
  - Safety issue
  - Science beyond self-heating phenomenon:

Heat dissipation  
Highly size dependent



Heat generation  
Exothermic reaction(s)



## ■ Industrial safety issue



(Esbjerg, Danemark, 1998)

70 000 tonnes de pellets  
de bois

- The larger the system the more sensitive to self-heating and self-ignition (Franck-Kamenetskii 1969)
- Phenomenon observed with torrefied wood (Verhoeff et al. 2012)

## ■ Thesis scientific approach

### ➤ The larger the system

❖ ↗ ↗ Industrial issues

❖ ↘ ↘ Understanding and control of physicochemical phenomenon involved

### ➤ Multi-scale approach



mg

Powder

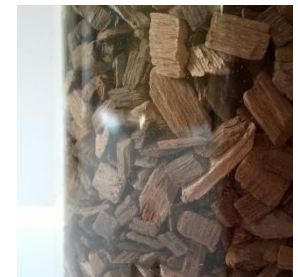
Reaction only



g

Particle

Diffusion + reaction



kg

Fixed bed particles

Advection + diffusion + reaction

## ■ Thesis scientific approach

### ➤ The larger the system

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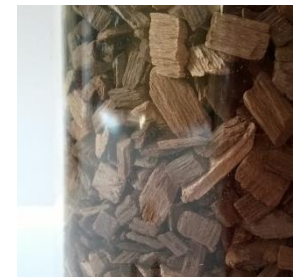
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kg

Fixed bed particles

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**Today's program: how to describe the reaction kinetic between oxygen and torrefied wood?**

## 1. Introduction

- a. Social context
- b. Scientific context

## 2. Bibliographic results

## 3. Experimental parts

- a. Protocol presentation
- b. Calorimetry, TGA and DSC results

## 4. Conclusion & perspectives

## ■ What does the literature teach us ?

### ➤ Coal industry: long time issue

- ❖ Reaction called « low – temperature oxidation »
- ❖ Related to mining and handling hazards

### ➤ General findings

Chemisorption of  $O_2$   
creation of surface oxides  
(Vastola et al. 1964)

Thermal decomposition  
of surface oxides  
(Marinov 1977)

$CO$  and  $CO_2$  are the  
main gaseous product  
(Gethner 1985)

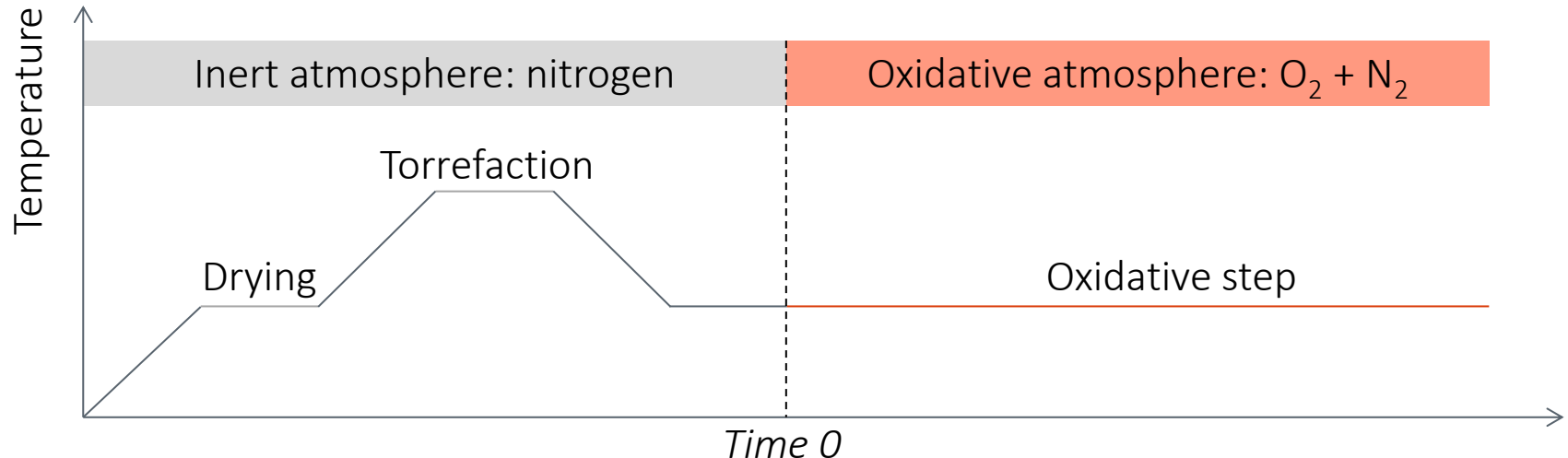
Complex reaction  
mechanism simplifies  
(Wang et al. 2003)

Reactive sites: carbon atoms  
limiting reagent  
(Teng & Hsieh 1999)



## ■ Classical protocol\*

- Raw material: beech wood powder (<math><80\ \mu\text{m}</math>)

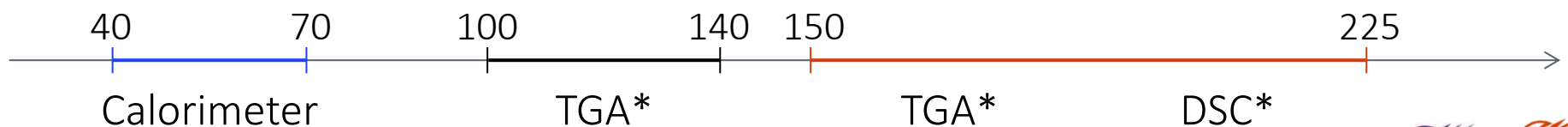


- Two severities of torrefaction

- ❖ Mild (240°C, 20 min), yield 86 +/- 1%
- ❖ Severe (290°C, 3 min), yield 68 +/- 2%

$$\text{Yield} = \frac{m_{\text{torrefied}}}{m_{\text{dry}}}$$

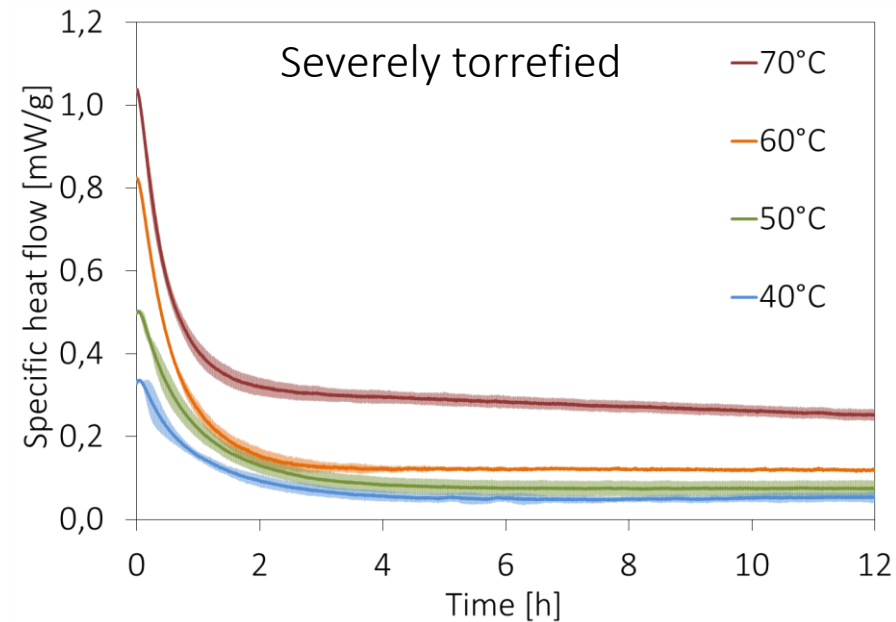
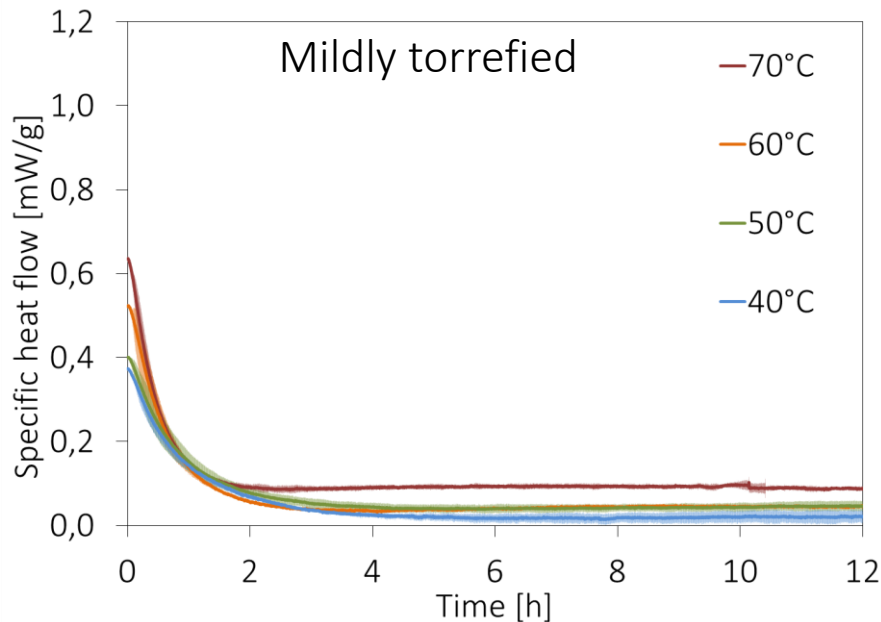
- Oxidative step temperature range [°C] & experimental devices



## ■ Calorimetric results, [40 ; 70] °C

### ➤ Specificity of the protocol

- ❖ Torrefaction ex situ
- ❖ Heat flow stabilized 10 hours under nitrogen flush then 12 hours under air flush



- ❖ Maximum heat flow followed by an exponential decay
  - Highest number of free reactive site at time 0 and consumption
- ❖ Increase with torrefaction severity
  - Higher propensity to self-heat and self-ignite

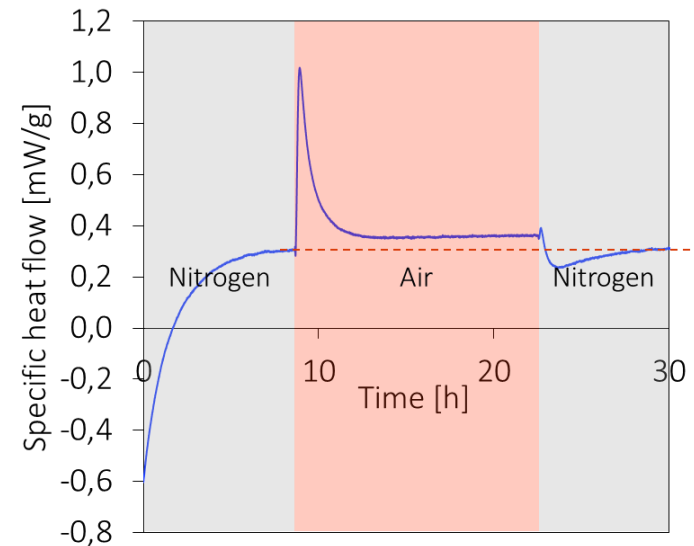
## ■ Why does the heat flow not go back to zero ?

### ➤ Diffusion ?

❖ Effective diffusion coefficient:

$$D_{O_2,eff} \sim \frac{L_c^2}{\tau_c} = \frac{(5 \mu m)^2}{10h} = 10^{-16} m^2 \cdot s^{-1}$$

### ➤ Experimental artefact ?

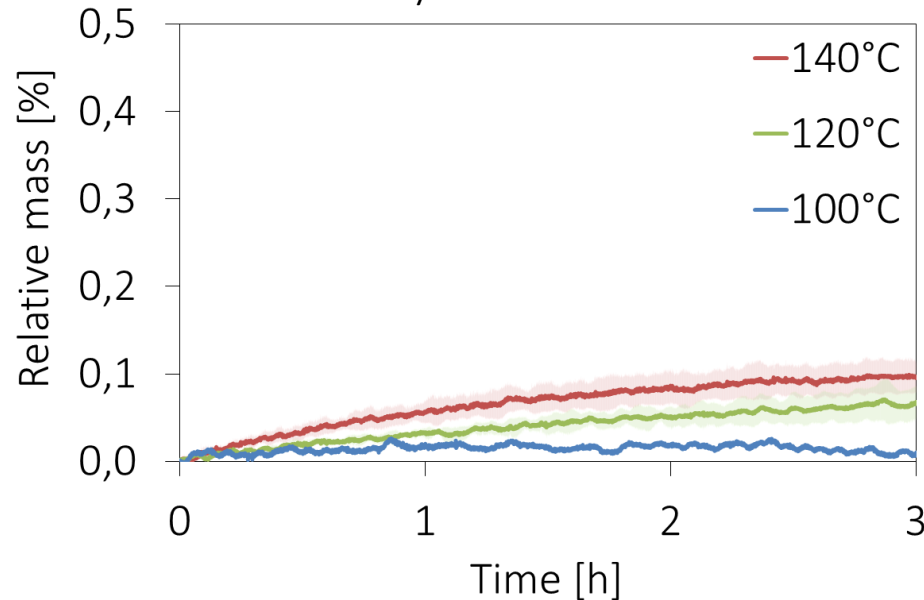


### ➤ Equilibrium between pyrolysis reactions and oxygen adsorption (Kaji et al. 1987)

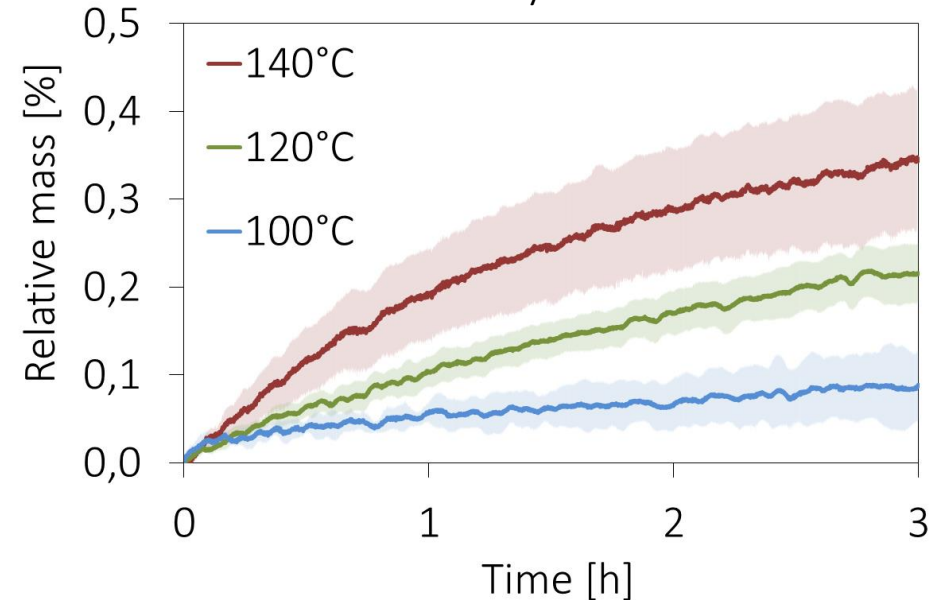
## ■ Small heat of physisorption involved

## ■ TGA results, [100 ; 140] °C

Mildly torrefied

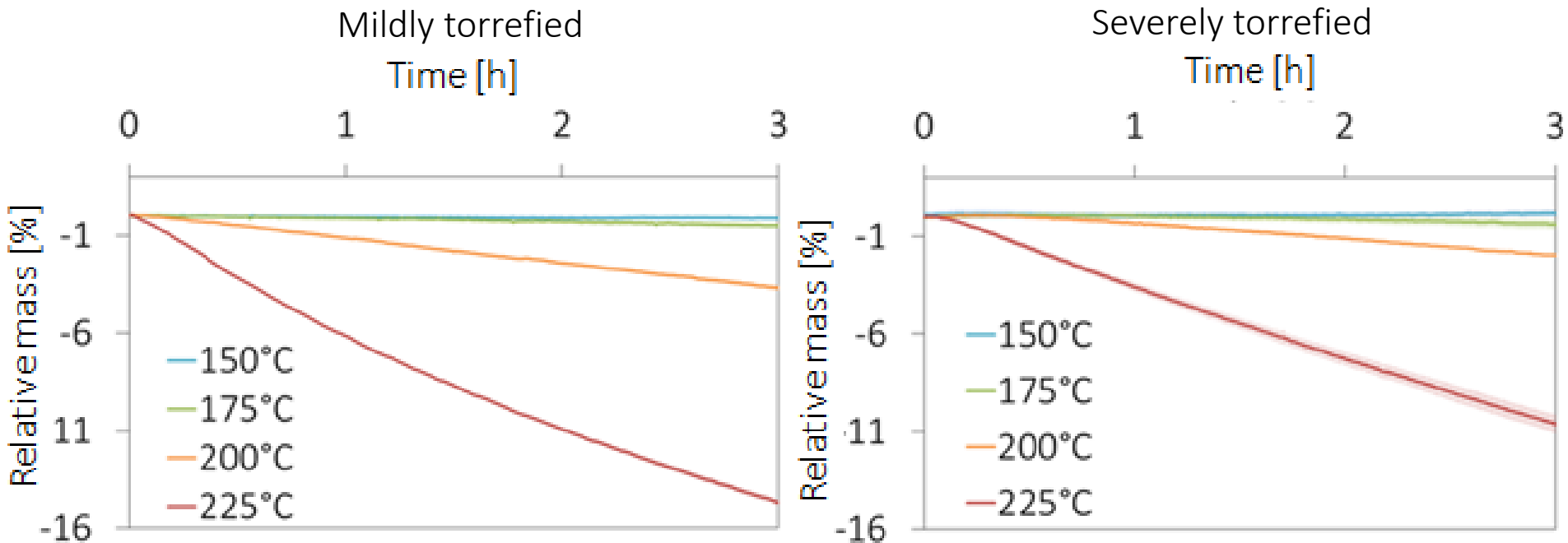


Severely torrefied



- ❖ Small amount of oxygen adsorbed on the wood surface
- ❖ Increase with severity of torrefaction
  - Higher number of free reactive sites
    - Increase of carbon content with torrefaction severity

## ■ TGA results, [150 ; 225] °C



❖ At temperature  $\approx 175^\circ\text{C}$  pyrolysis > adsorption

- Above  $200^\circ\text{C}$ , non-negligible mass loss involved

❖ Thermal degradation decreases with torrefaction severity

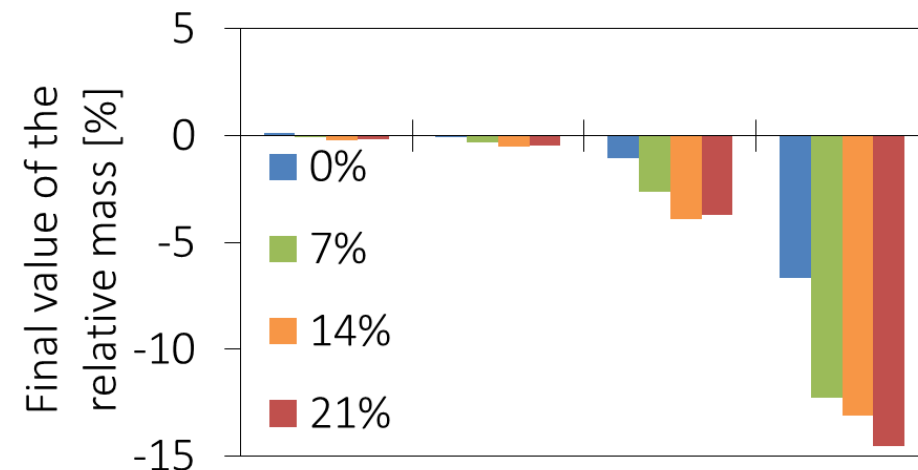
- Wood volatile matters decrease with torrefaction severity

## ■ TGA results: influence of oxygen concentration

Mildly torrefied

Oxydative step temperature [°C]

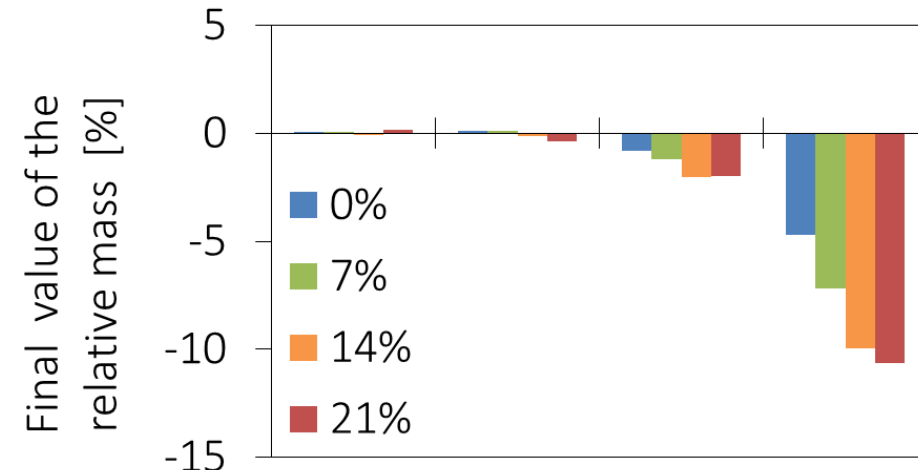
150 175 200 225



Severely torrefied

Oxidative step temperature [°C]

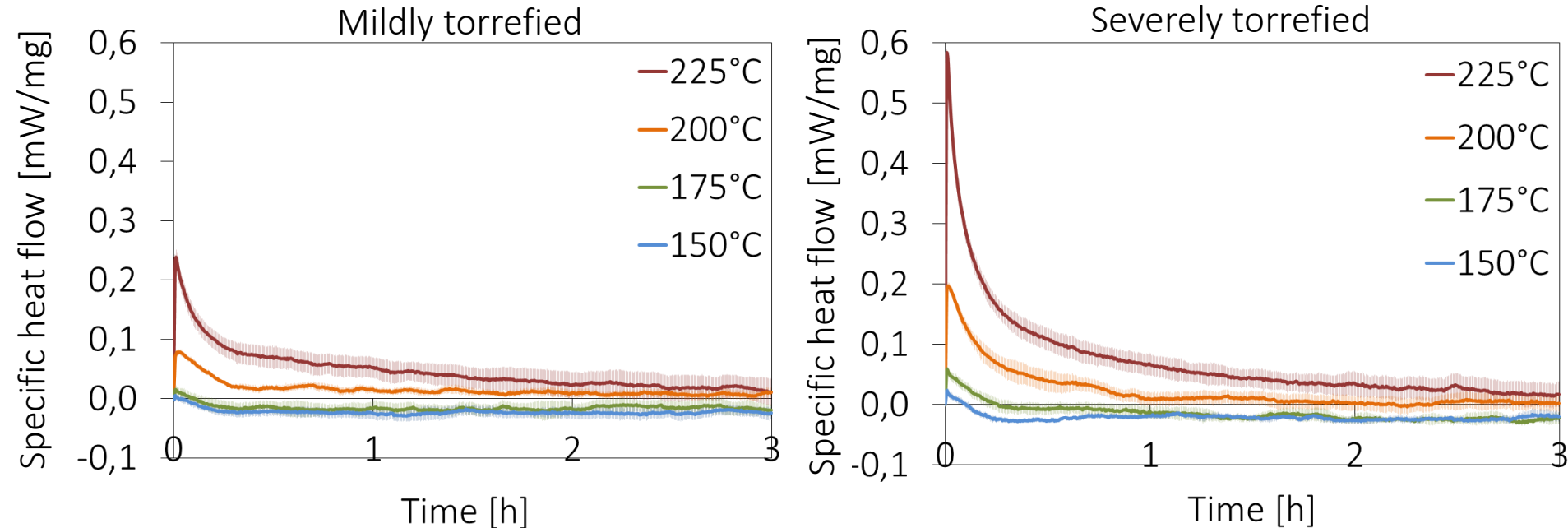
150 175 200 225



### ❖ Thermal degradation enhanced by oxygen

- Pyrolysis reactions of surface oxides: thermal decomposition
- Pyrolysis reactions of torrefied wood: thermal cracking

## ■ DSC results, [150 ; 225] °C



### ❖ Exothermic overall heat flow but thermal degradation (TGA)

- Pyrolysis reactions govern the mass
- Adsorption reactions govern the heat flow

### ❖ The heat flow goes back to zero

- Endothermic pyrolysis reactions enhanced

## ■ Conclusion

➤ How to describe the low-temperature oxidation of torrefied wood ?

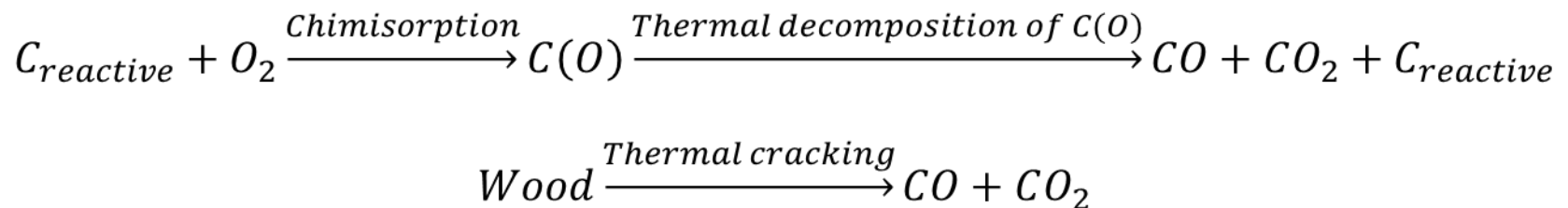
❖ Similarities between low-temperature oxidation of torrefied wood and coal:

- Chemisorption describes well the heat involved
- Pyrolysis reactions of surface oxides

❖ Difference

- Pyrolysis reactions of torrefied wood at lower temperature

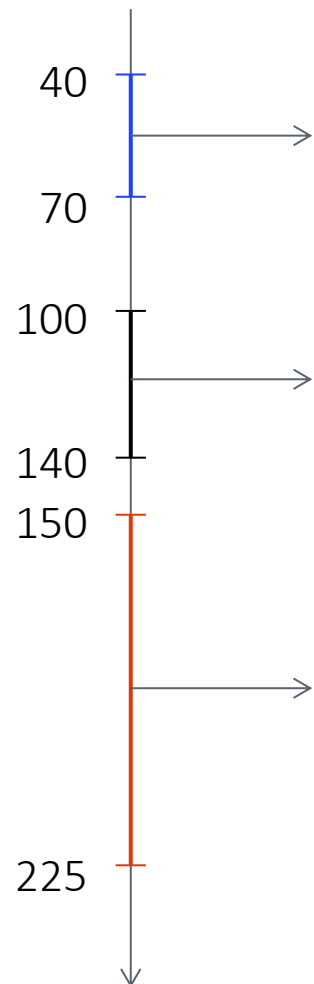
❖ Reactions





## ■ On going work: kinetic modelling

Temperature  
range [°C]



### 1. Modelling adsorption at very low temperature

- ❖ Based on calorimetric results
- ❖ Pyrolysis reactions neglected

### 4. Verify the reaction kinetics

### 2. Modelling thermal cracking

- ❖ Based on TGA and DSC results without oxygen

### 3. Modelling thermal decomposition

- ❖ Based on TGA and DSC results with oxygen



Thank you for your attention  
Questions are welcome

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