Prediction accuracy in modelling beech wood pyrolysis at different temperatures using a comprehensive, CFD-based single particle pyrolysis model

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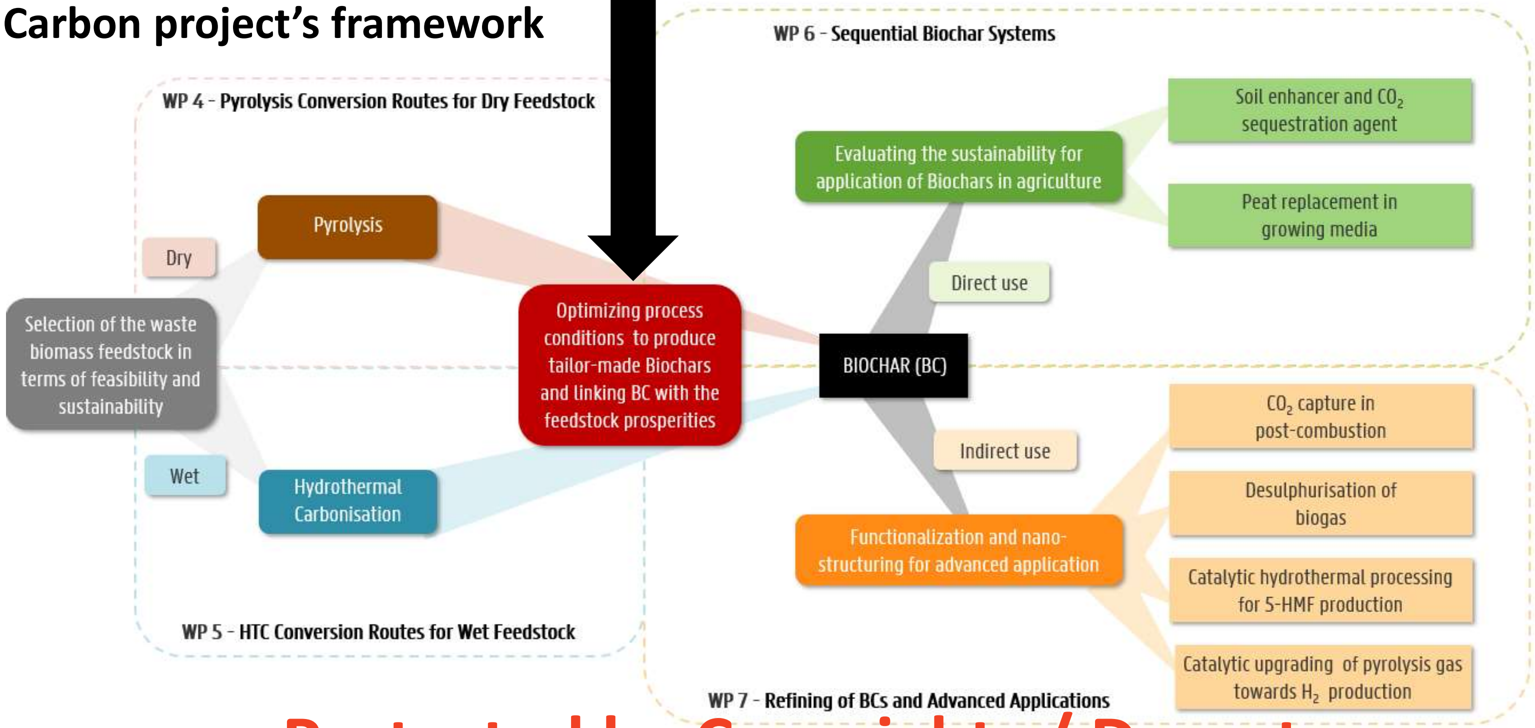
ESR #4 - Przemyslaw Maziarka – role in the Project

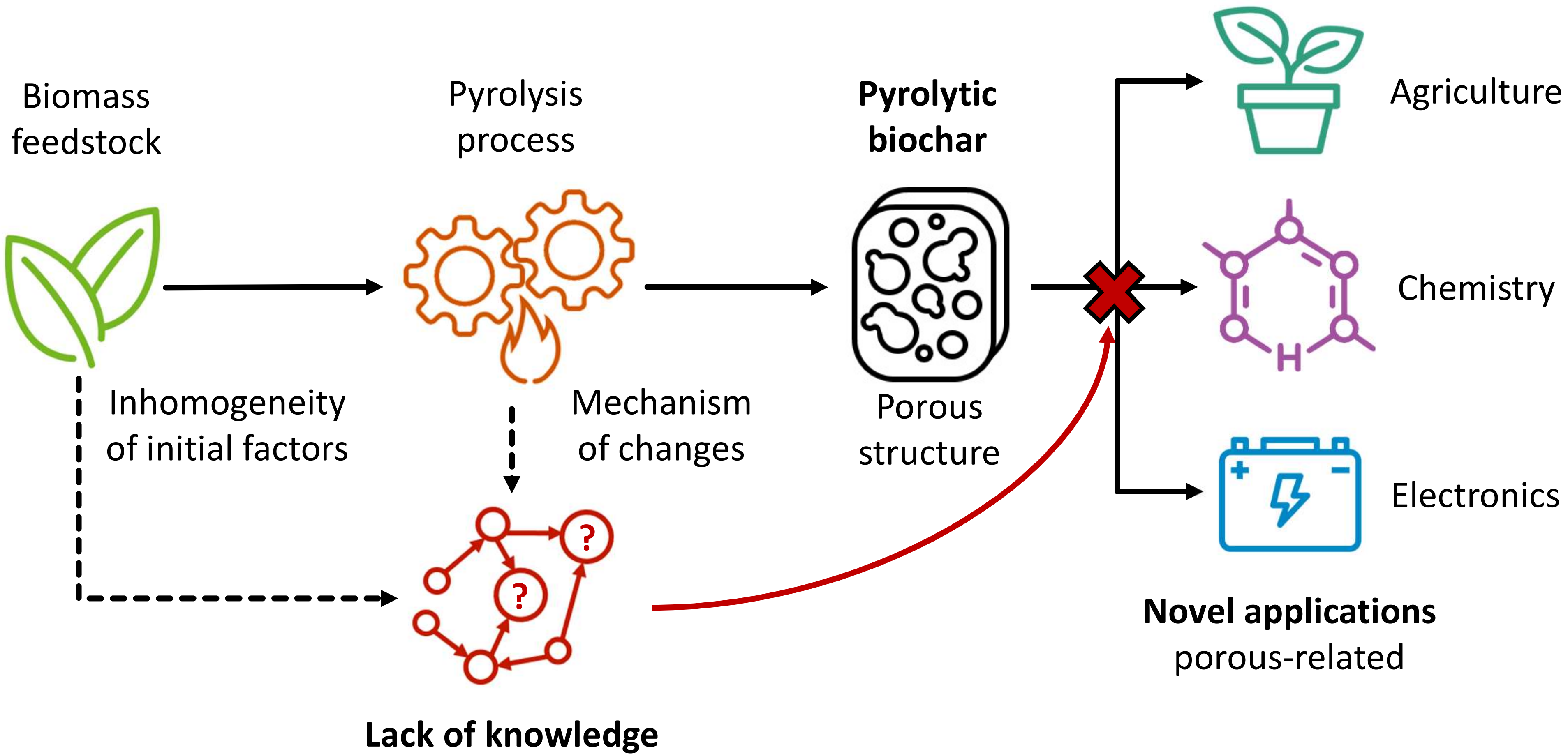
Role in the Project

Development of a comprehensive pyrolysis/carbonisation model to predict the properties of co-produced biomass-derived carbon (BC) and bio-oil

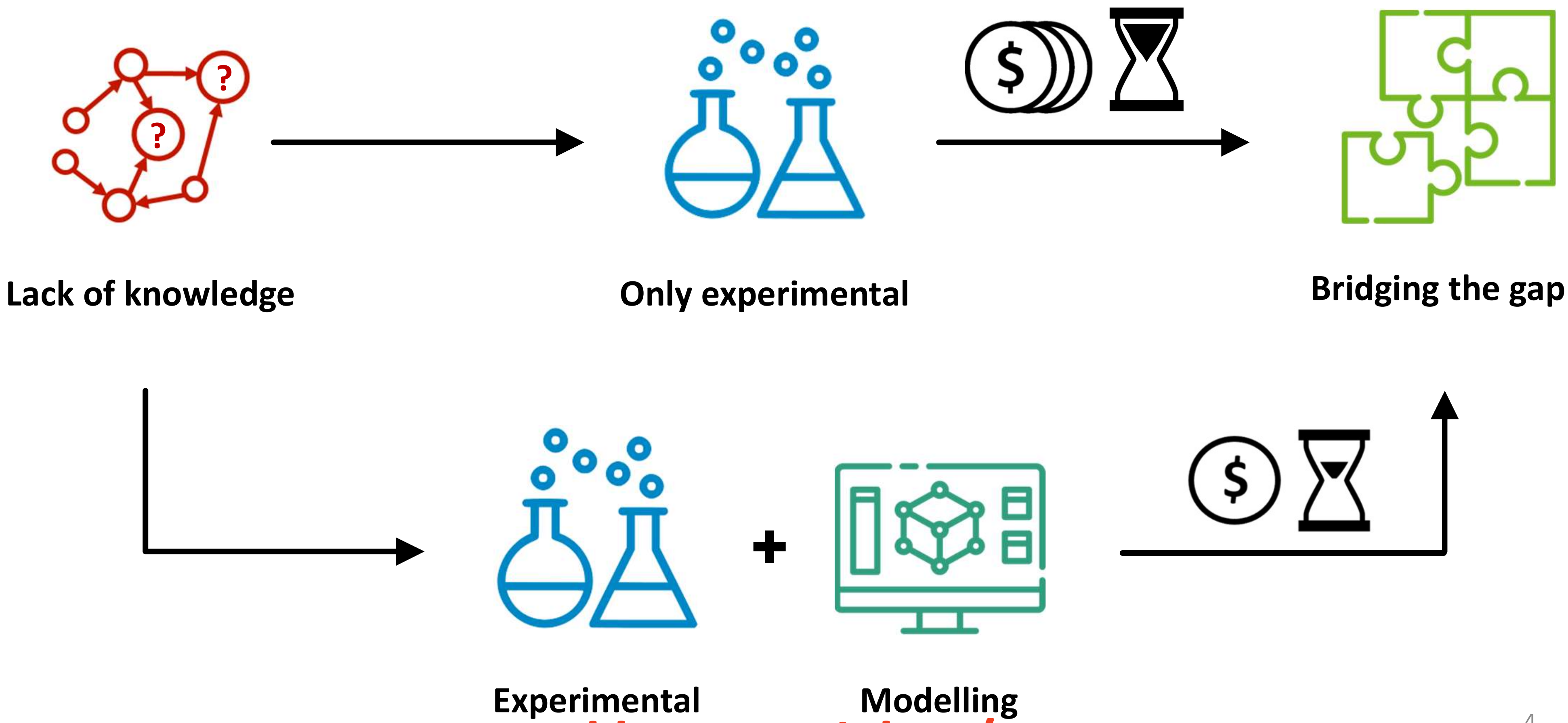
GreenCarbon project's framework



Biochar production and its porous-related applications



Biochar production and its porous-related applications



Outline

1. Model preparation with external experimental data

- Relevance of the wood's anisotropy
  Lu et al. (2008)
- Selection of the biomass degradation kinetic scheme
  Bennadji et al. (2014)
- Validation of the model on broad range of the cylinder size and pyro. Temperature
  Atreya et al. (2017)

2. Data acquisition in experimental Single Particle Pyrolysis

- Range of the experimental work and investigation procedure
- Overview of the results obtained from experimental work

3. Validation of the model with experimentally obtained data

- Prediction accuracy of the Center Temperature and Mass Loss profile
- Prediction accuracy of yields of lumped products
- Improvements to implement

1. Model preparation with external experimental data

Model in brief – parameters and relations

Fundamental relations between parameters:

Governing equations

$$\frac{\partial T}{\partial t}\left(<\rho_S>\boldsymbol{C_{P,S}}+\varepsilon_G<\rho_G>^G\boldsymbol{C_{P,G}}\right)+\nabla T\left(\varepsilon_G\sum_{i=1}^{N}<u_i\rho_i>\boldsymbol{C_{P,i}}\right)=\nabla\left(\boldsymbol{\lambda_{eff}}\nabla T\right)+\mathbf{Q}$$

Auxiliary equations

$$\dot{\omega}_i=<\rho_i>A_i e^{\left(-\frac{E_a}{RT}\right)}$$

Boundary conditions

$$\nabla\left(\lambda_{eff}\nabla T\right)|_{x=x_B}=\boldsymbol{h_T}\left(\boldsymbol{T_{flow,\infty}}-T|_{x=x_B}\right)+\sigma\boldsymbol{\omega}\left(\boldsymbol{T^4_{wall}}-T^4|_{x=x_B}\right)$$

Model specific parameters:

- Heat transfer conditions
- Fluid flow conditions
- Mass diffusion
- Reaction kinetics
- Reactions heat
- Compounds molar mass
- Heat capacities
- Thermal conductivities
- Fluid Viscosity
- True density
- Porosity
- Permeabilities
- Pore sizes
- Bio-composition (solid)*
- Shrinking factors*

Chemical and thermo-physical parameters relations have to **directly correspond to the modelled scenario**

Model in brief - details (all cylinders)

1. Study - Anisotropy of wood
based on Lu et al. (2008)

- How relevant is the wood's anisotropy in model?

2. Study - Biomass degradation kinetics
based on Bennadji et al. (2014)

- Which kinetic scheme is the most accurate for large particle pyrolysis?

3. Study - Accuracy over broad range
based on Atreya et al. (2017)

- Is the model accurate for broad range of pyro. temp. and particle size?

Parameter	Symbol	Unit	Value
Particle	*Cylinder, moist poplar wood*		
Diameter	D	[mm]	9.5
Height	H	[mm]	38
Moisture content	MC	[-]	0.06 / 0.4
Bulk density (dry)	$<\rho_S>$	[kg/m³]	580
Thermal conductivity			
Biomass (L)	$\lambda_{Biomass,L}$	[W/(m·K)]	0.315
Biomass (R)	$\lambda_{Biomass,R}$	[W/(m·K)]	0.150
Char (L)	$\lambda_{Char,L}$	[W/(m·K)]	0.215
Char (R)	$\lambda_{Char,R}$	[W/(m·K)]	0.100
Permeability			
Biomass (L)	$K_{Biomass,L}$	[m²]	$1 \cdot 10^{-14}$
Biomass (R)	$K_{Biomass,R}$	[m²]	$5 \cdot 10^{-16}$
Char (L)	$K_{Char,L}$	[m²]	$5 \cdot 10^{-13}$
Char (R)	$K_{Char,R}$	[m²]	$1 \cdot 10^{-13}$
Boundary temperature			
Gas	T_{Gas}	[°C]	**780**
Wall	T_{Wall}	[°C]	**960**
Initial	T_{Ini}	[°C]	25

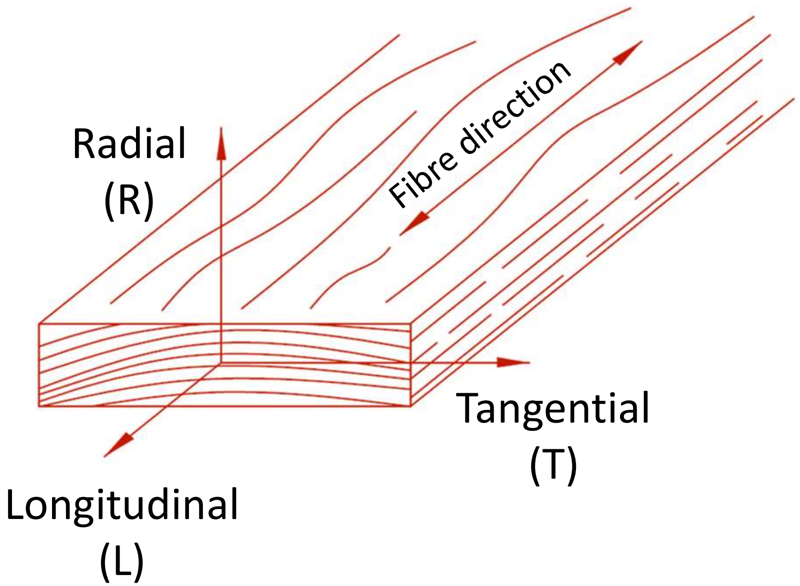
Model specific parameters

Parameter	Symbol	Unit	Value
Particle	Cylinder, dry poplar wood		
Diameter	D	[mm]	19.05
Height	H	[mm]	40
Moisture content	MC	[-]	0
Bulk density (dry)	$<\rho_S>$	[kg/m³]	500
Biocomponents conc.			
Cellulose (CELL)	c_{CELL}	[wt. %]	50.50
Hemicellulose (HCE)	c_{HCE}	[wt. %]	29.55
H-rich lignin (LIG-H)	c_{LIGH}	[wt. %]	2.59
O-rich lignin (LIG-O)	c_{LIGO}	[wt. %]	7.38
C-rich lignin (LIG-C)	c_{LIGC}	[wt. %]	9.98
Secondary charring param.			
Cellulose	x_{CELL}	[-]	0.20
Hemicellulose	x_{HCE}	[-]	0.25
Lignin	x_{LIG}	[-]	0.35
Metaphase	$x_{G[X]}$	[-]	0.40
Thermal conductivity			
Biomass (L)	$\lambda_{Biomass,L}$	[W/(m·K)]	0.255
Biomass (R)	$\lambda_{Biomass,R}$	[W/(m·K)]	0.125
Char (L)	$\lambda_{Char,L}$	[W/(m·K)]	0.105
Char (R)	$\lambda_{Char,R}$	[W/(m·K)]	0.071
Permeability			
Biomass (L)	$K_{Biomass,L}$	[m²]	$1 \cdot 10^{-14}$
Biomass (R)	$K_{Biomass,R}$	[m²]	$1 \cdot 10^{-16}$
Char (L)	$K_{Char,L}$	[m²]	$5 \cdot 10^{-13}$
Char (R)	$K_{Char,R}$	[m²]	$5 \cdot 10^{-14}$
Boundary temperature			
Gas	T_{Gas}	[°C]	**418**
Wall	T_{Wall}	[°C]	**418**
Initial	T_{Ini}	[°C]	95

Parameter	Symbol	Unit	Value
Particle	Cylinder, dry maple wood		
Diameters	$D1$	[mm]	10
	$D2$		15
	$D3$		20
Height	H	[mm]	20
Moisture content	MC	[-]	0
Bulk density (dry)	$<\rho_S>$	[kg/m³]	630
Biocomponents conc.			
Cellulose (CELL)	c_{CELL}	[wt. %]	42.20
Hemicellulose (HCE)	c_{HCE}	[wt. %]	32.30
H-rich lignin (LIG-H)	c_{LIGH}	[wt. %]	16.51
O-rich lignin (LIG-O)	c_{LIGO}	[wt. %]	5.59
C-rich lignin (LIG-C)	c_{LIGC}	[wt. %]	3.30
Thermal conductivity			
Biomass (L)	$\lambda_{Biomass,L}$	[W/(m·K)]	0.255
Biomass (R)	$\lambda_{Biomass,R}$	[W/(m·K)]	0.115
Char (L)	$\lambda_{Char,L}$	[W/(m·K)]	0.105
Char (R)	$\lambda_{Char,R}$	[W/(m·K)]	0.081
Permeability			
Biomass (L)	$K_{Biomass,L}$	[m²]	$1 \cdot 10^{-14}$
Biomass (R)	$K_{Biomass,R}$	[m²]	$1 \cdot 10^{-16}$
Char (L)	$K_{Char,L}$	[m²]	$5 \cdot 10^{-13}$
Char (R)	$K_{Char,R}$	[m²]	$5 \cdot 10^{-14}$
Boundary temperature			
Gas	$T_{Gas,500\,°C}$	[°C]	**494 ± 13**
	$T_{Gas,610\,°C}$		**603 ± 6**
	$T_{Gas,720\,°C}$		**714 ± 8**
	$T_{Gas,840\,°C}$		**838 ± 18**
Wall	$T_{Wall,500\,°C}$	[°C]	**509 ± 13**
	$T_{Wall,610\,°C}$		**618 ± 6**
	$T_{Wall,720\,°C}$		**726 ± 8**
	$T_{Wall,840\,°C}$		**850 ± 18**
Initial	T_{Ini}	[°C]	40

1. Anisotropy of wood - base

Anisotropic structure of wood



λ_S - thermal conductivity solid

K - permeability gas and liquid

Longitudinal ≠ Radial ≈ Tangential

Investigated scenarios

Anisotropy

$$A = \begin{bmatrix} A_{r,r} & 0 & 0 \\ 0 & A_{\varphi,\varphi} & 0 \\ 0 & 0 & A_{z,z} \end{bmatrix}$$

λ_S and K different in L and R direction

$A \in [K, \lambda_S]$

Isotropy

$$A_{ISO} = \left(A_{r,r} \cdot A_{\varphi,\varphi} \cdot A_{z,z}\right)^{1/3}$$

λ_S and K averaged and same in L and R direction

↑

If accurate, 1D model is sufficient

1. Anisotropy of wood - results

Temperature and mass loss profile

- More accurate for the anisotropic
- Thermal conductivity directional dependence - **relevant**

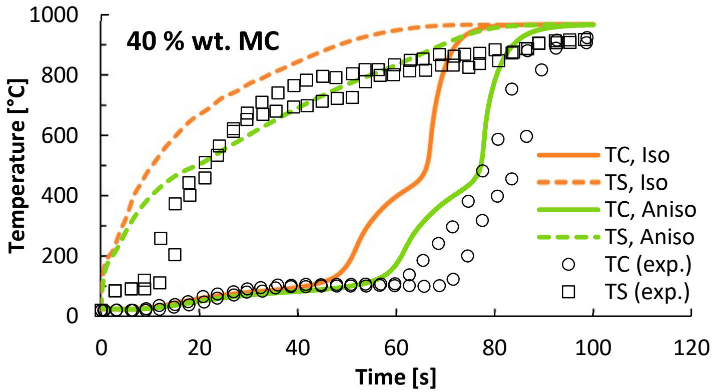
Intrinsic gas velocity distribution

- Anisotropic model profile presents realistic velocity distribution
- Permeability directional dependency - **relevant**

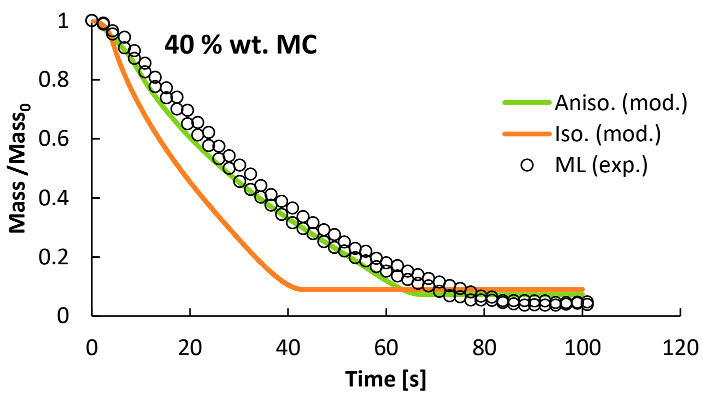
- **Anisotropy of wood have to be implemented in models**

- **The 2D model is the lowest dimension model**

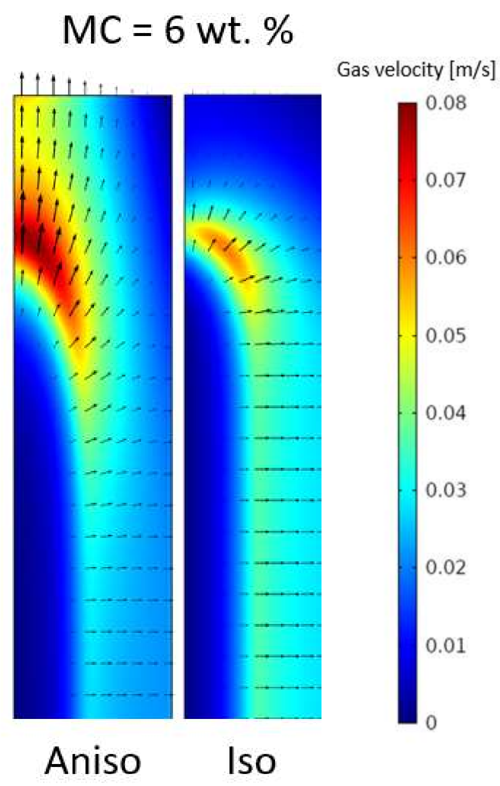
Center (TC) and surface (TS) temperature profile



Mass loss profile profile



Gas velocity distribution (eta = 70%)



(exp.) - Lu et al. (2008)

2. Biomass degradation kinetics - base

Simple

Biomass: bulk compound

Products: Gas, Tar and Char

Detailed

Biomass: bio-components mix (lignin in 3 artificial forms)

Products: numerous volatile compounds, char as carbon and metaphase traps

Shafizadeh and Chin's

(Shafizadeh and Chin, 1978)

Reactions: 3

Compounds: 4

Ranzi

(Debiagi et al., 2018)

Reactions: 25

Compounds: 48

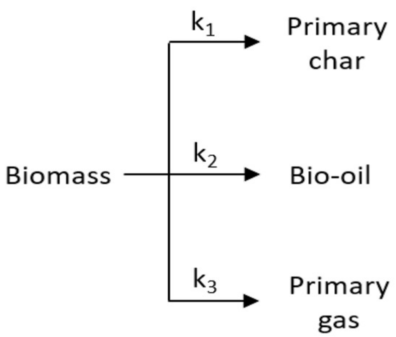
Ranzi Anca-Couce (RAC)

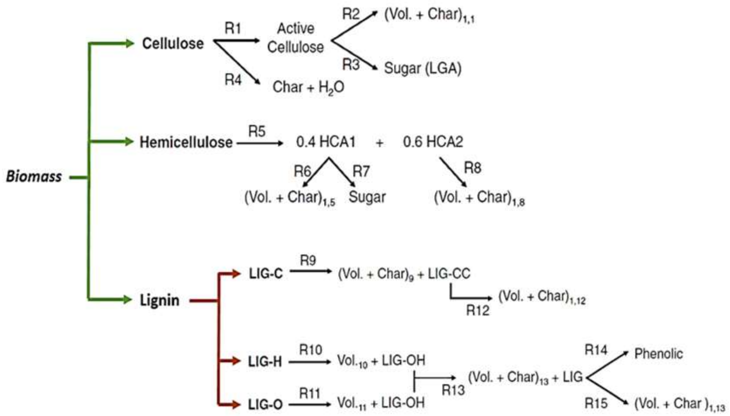
(Anca-Couce et al., 2017)

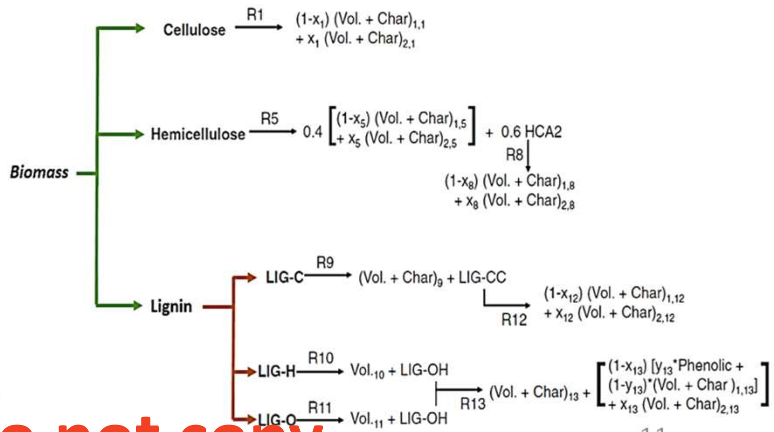
Reactions: 24

Compounds: 33

+ 4 parameters of secondary charring "x"







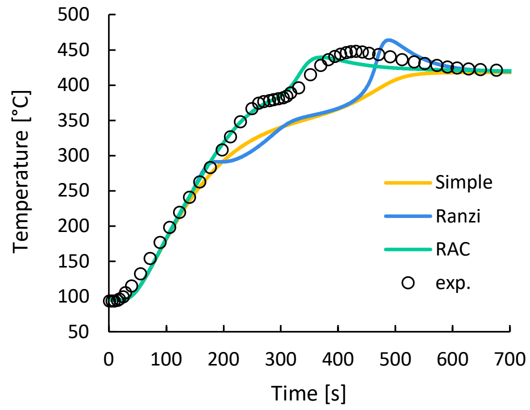
2. Biomass degradation kinetics - results

Simple vs Detailed (TC, lumped yields)
- RAC > Ranzi ≈ Simple
- Simple = no detailed release profiles

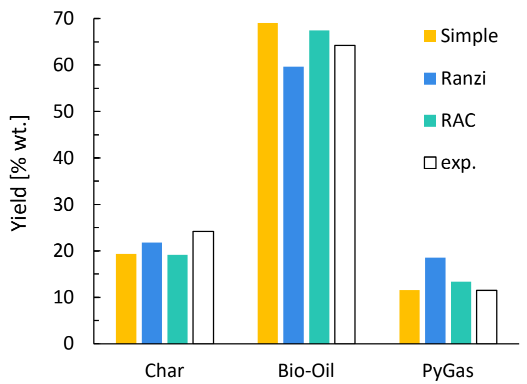
Ranzi vs RAC
- RAC > Ranzi - TC profile production, lumped yields, release profiles (MeALD and EtAC)

- **Simple scheme - not sufficient nor accurate for detailed study**
- **RAC > Ranzi in the accuracy of the pyrolysis outcome prediction**

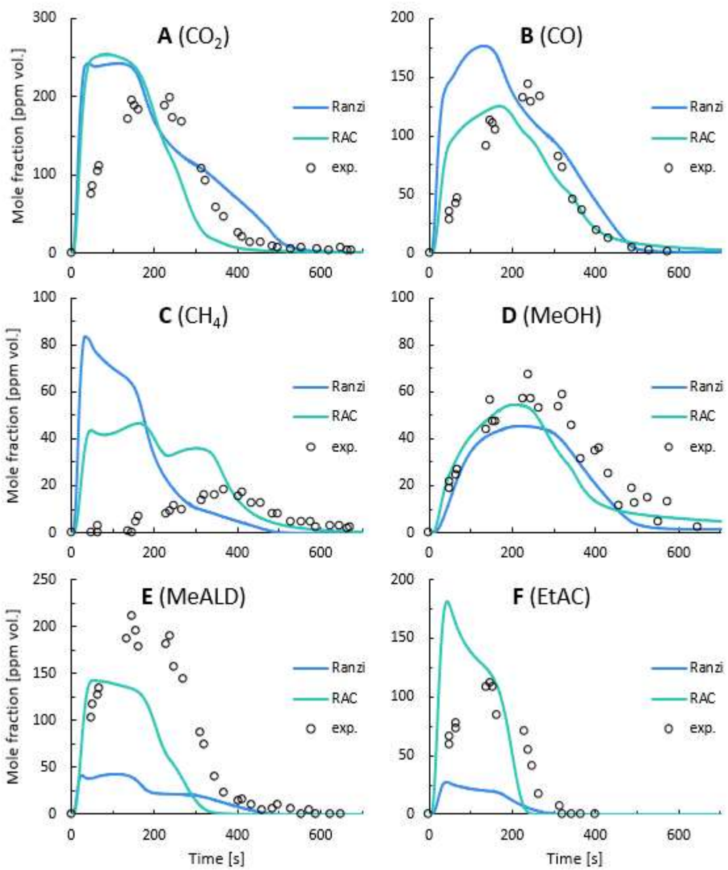
Center temperature profile



Yields of lumped products



Release profile of specific compounds



(exp.) - Bennadji et al. (2014)

3. Broad range of parameters - base

Model performance was investigated against different:
Pyrolysis temperature and particle size (diameter)

Temperatures (4) **×** **Particle sizes (3)** **=** **Total scenarios (12)**

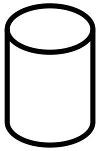
500 °C

610 °C

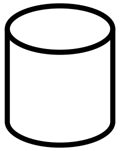
720 °C

840 °C

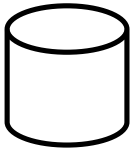
D = 10 mm
Ø10x20mm



D = 15 mm
Ø15x20mm



D = 20 mm
Ø20x20mm



Secondary charring parameters as the function for each scenario

Parameter	Unit	Relation
x_{CELL}	[-]	$0.008\ L_{\parallel} - 0.2$
x_{HCE}	[-]	$0.016\ L_{\parallel} - 0.2$
x_{LIG}	[-]	$0.5645 - 0.0005\ T_{END}$
$x_{G[X]}$	[-]	$0.5645 - 0.0005\ T_{END}$

3. Broad range of parameters - results

Temperature center profile (all sizes)

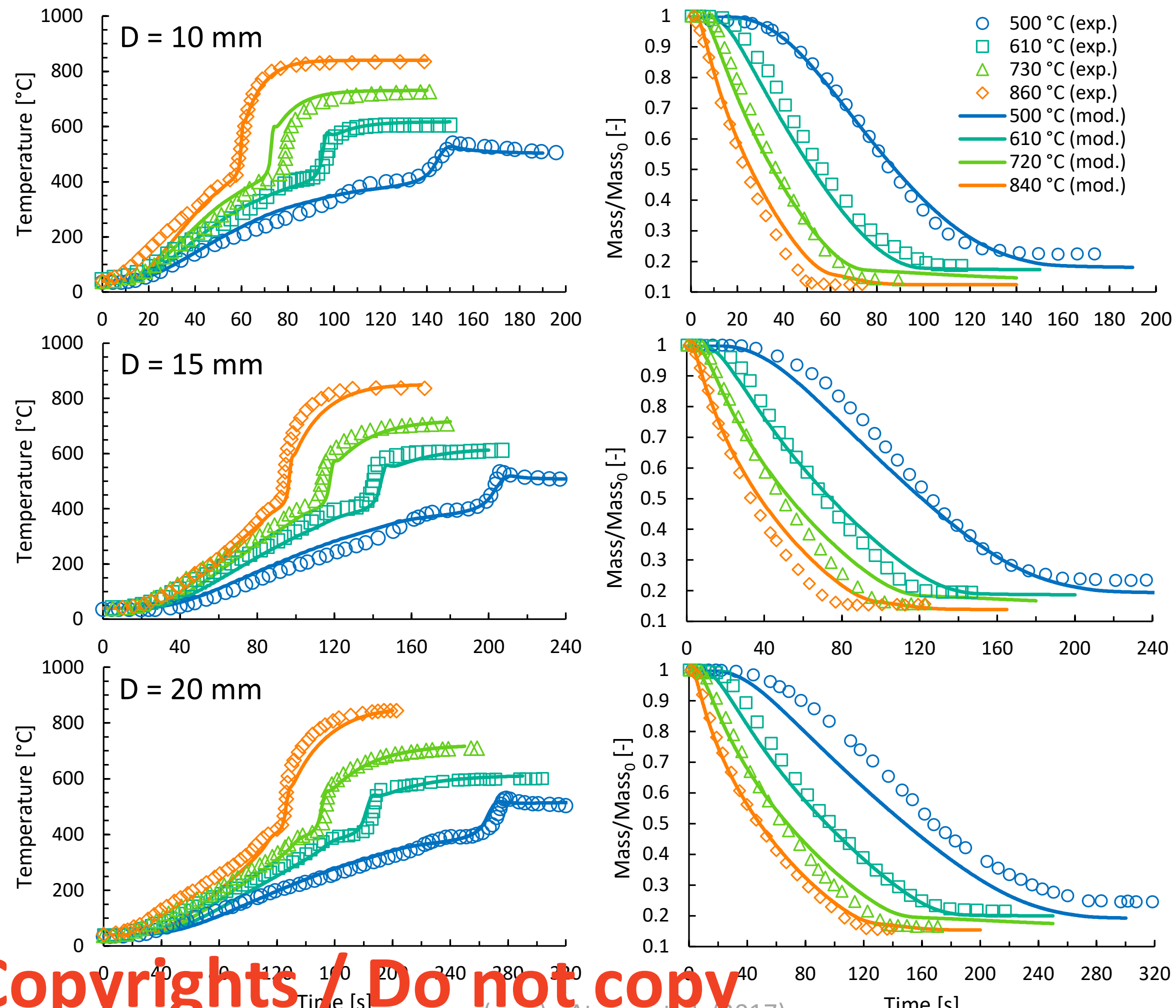
- Very accurate perdition for: **500 °C**, above, lack of fit in the initial stage of conversion
- Accurate perdition in the later stage for: **610 °C**, **720 °C** and **840 °C**

Mass loss profile (all sizes)

- Accurate perdition for: **610 °C** and **840 °C**
- Moderate accuracy for:
  500 °C - char yield under-predicted
  720 °C - char yield over-predicted

- **Satisfactory accuracy of TC and mass loss of the model over broad range of the parameters**
- **Model can be used for further the development**

Center temperature and mass loss profile from 12 scenarios



(exp.) - Atreya et al. (2017)

2. Data acquisition in experimental Single Particle Pyrolysis

Experimental - data matrix and procedure

Matrix of pyrolysis experiments

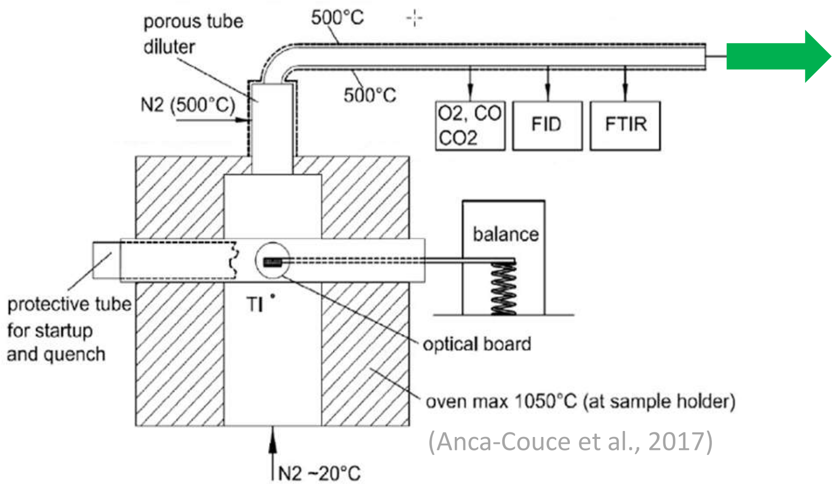
Particles used for pyrolysis
- Beech wood, drilled till center
- Dimeter = 8 mm
- Height = 10 mm

Pyrolysis temperature
- **300 °C**
- **400 °C**
- **500 °C**
- **700 °C**
- **900 °C**

Repetitions of vapours analyses
- 3x for light vapours (online)
- 3x for heavy vapours collect. (tar protocol)

6 reparations per 1 temp. point

Scheme of SPR at BEST GmbH



(Anca-Couce et al., 2017)

Direct, real-time measurement
(model validation data)
- Temperature center and surface (x6)
- Mass loss (x6)
- Light compounds release (x3):
- TCD (2): CO_2, CO
- FT-IR (15): CO_2, CO, methane, ethene, acetylene, propane and propene, acetic acid, lactic acid, formaldehyde, acetaldehyde, methanol, ethanol, furfural, and water

Secondary analysis on collected samples
(model expansion data)

Char particles (x6):
- CHNS
- True density change
- Shrinking factors
- Porosity
- Pore size distribution

Heavy condensables (x3):
- CHNS
- GC/MS-FID

Experimental - reactor

Single particle reactor

Particle appearance pre/post

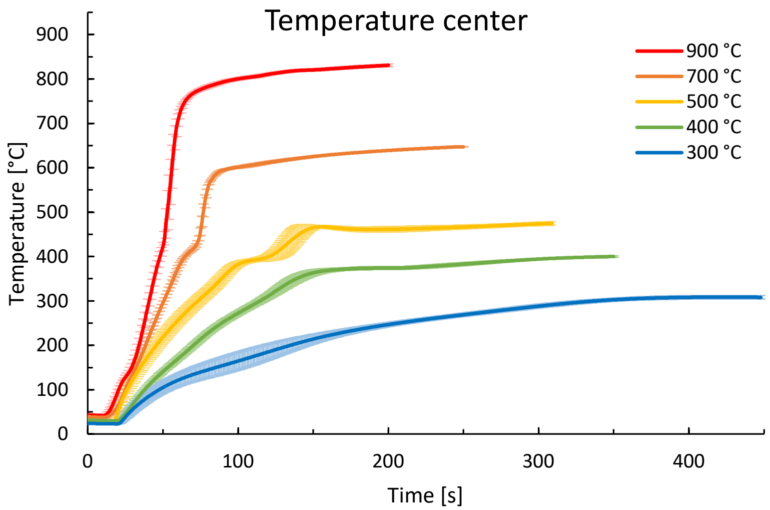
Experimental – results overview

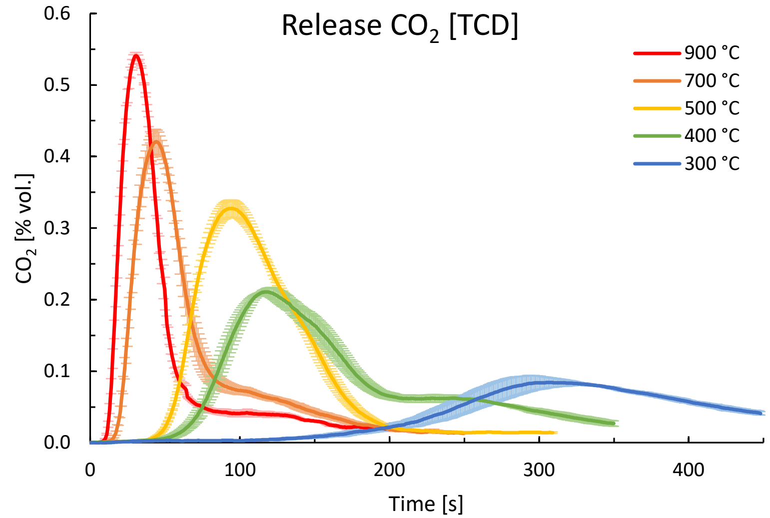
Average from:
- at least 3/6 measurement for TC and mass loss profile
- at least 2/3 measurements for the vapors release profile

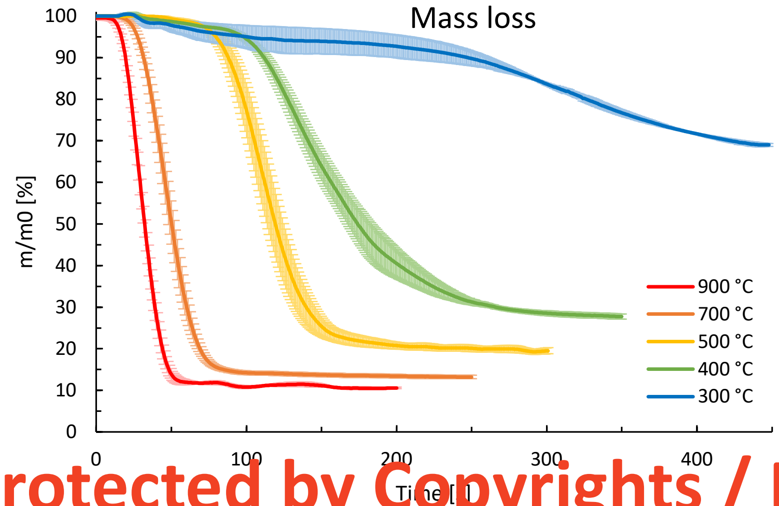
TC and mass loss profile:
- Very good repeatability, low standard deviation

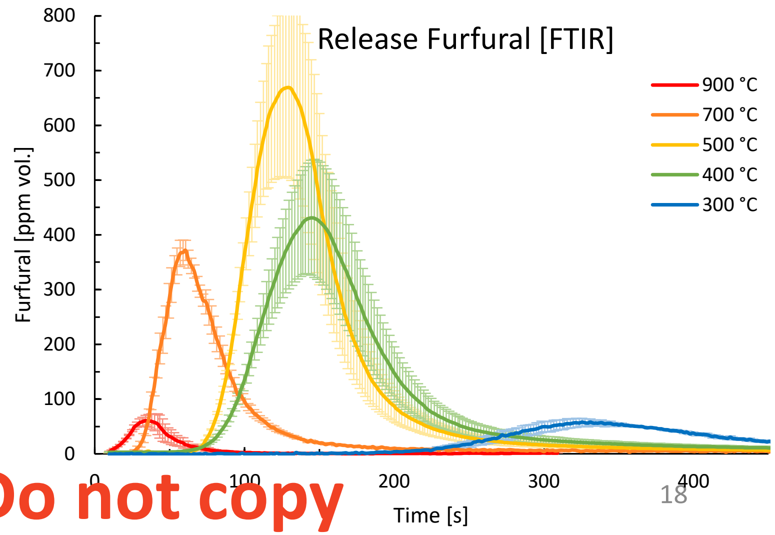
Release profile of permanent gases:
- Very good repeatability, low standard deviation

Release profile of light condensables:
- Good repeatability, noticeable deviation at peak





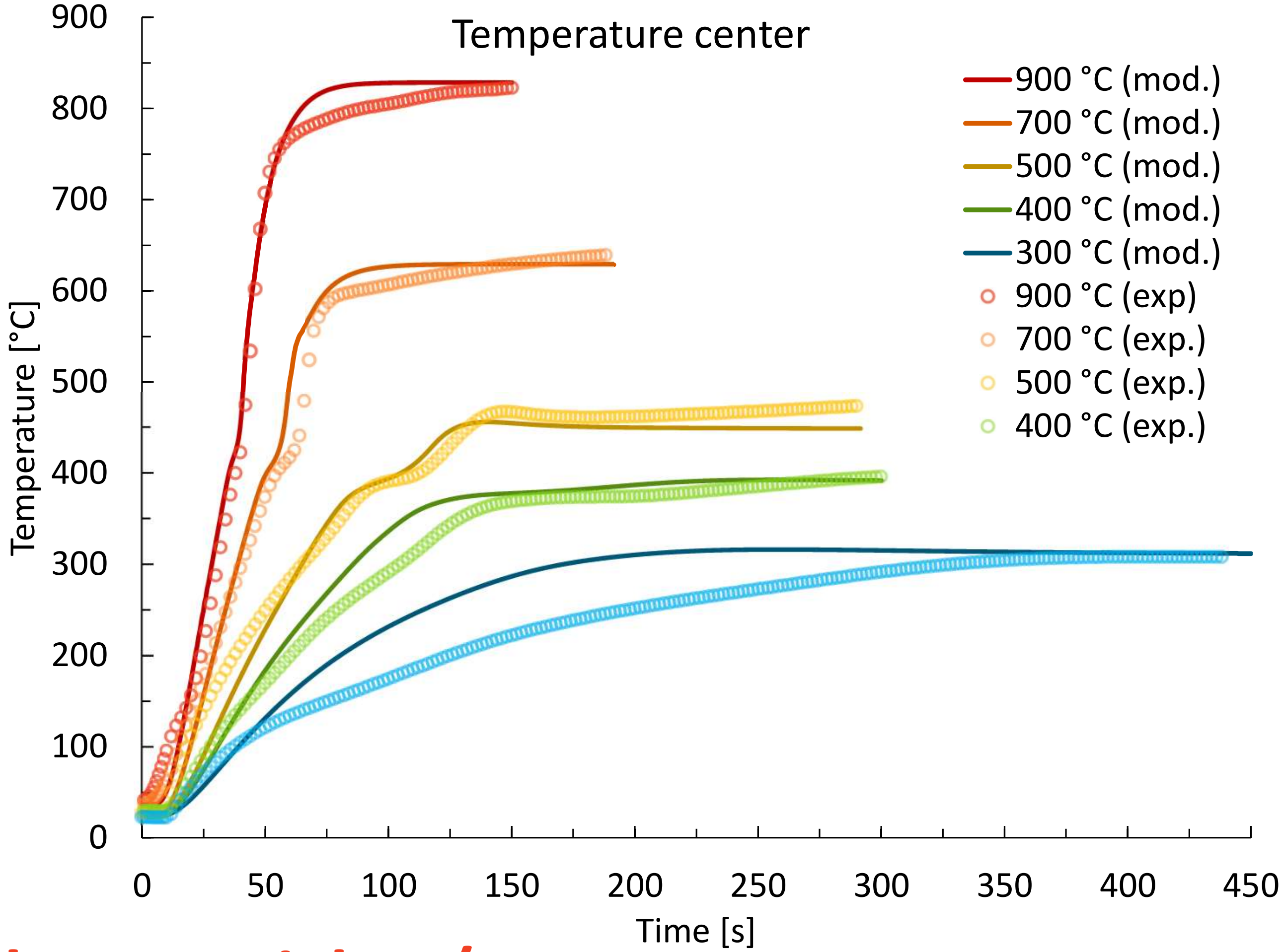




3. Validation of the model with experimentally obtained data

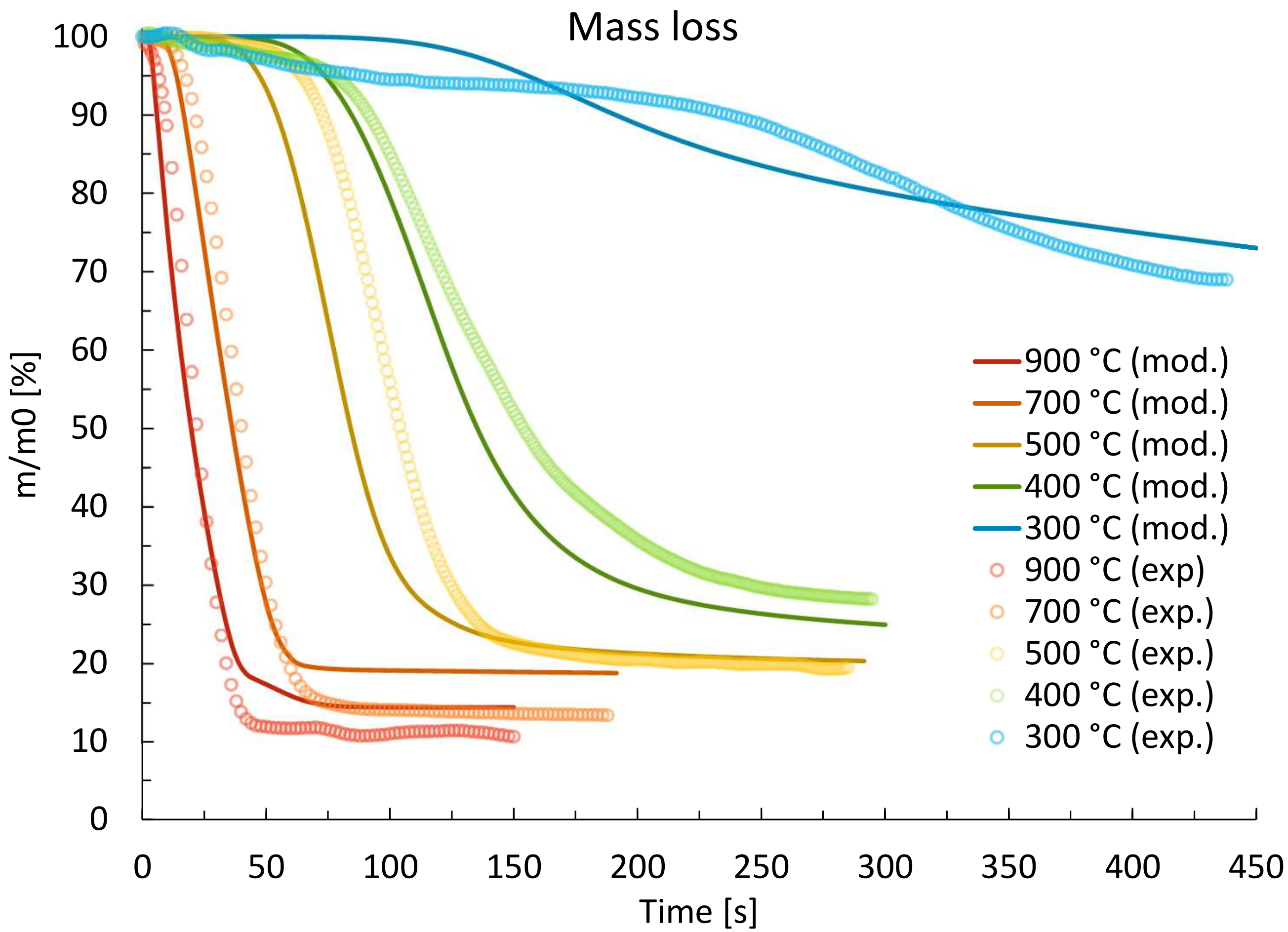
Model validation - center temperature profile fit

- Model satisfactorily well predicts the center temperature profile
- The model show moderate fit to the 400 °C profile and poor fit to profile from 300 °C
- For profiles above 400 °C model show good fit in the late stage of the conversion
- As expected, for profiles above 400 °C in the initial stage the model lacks of the precise fit



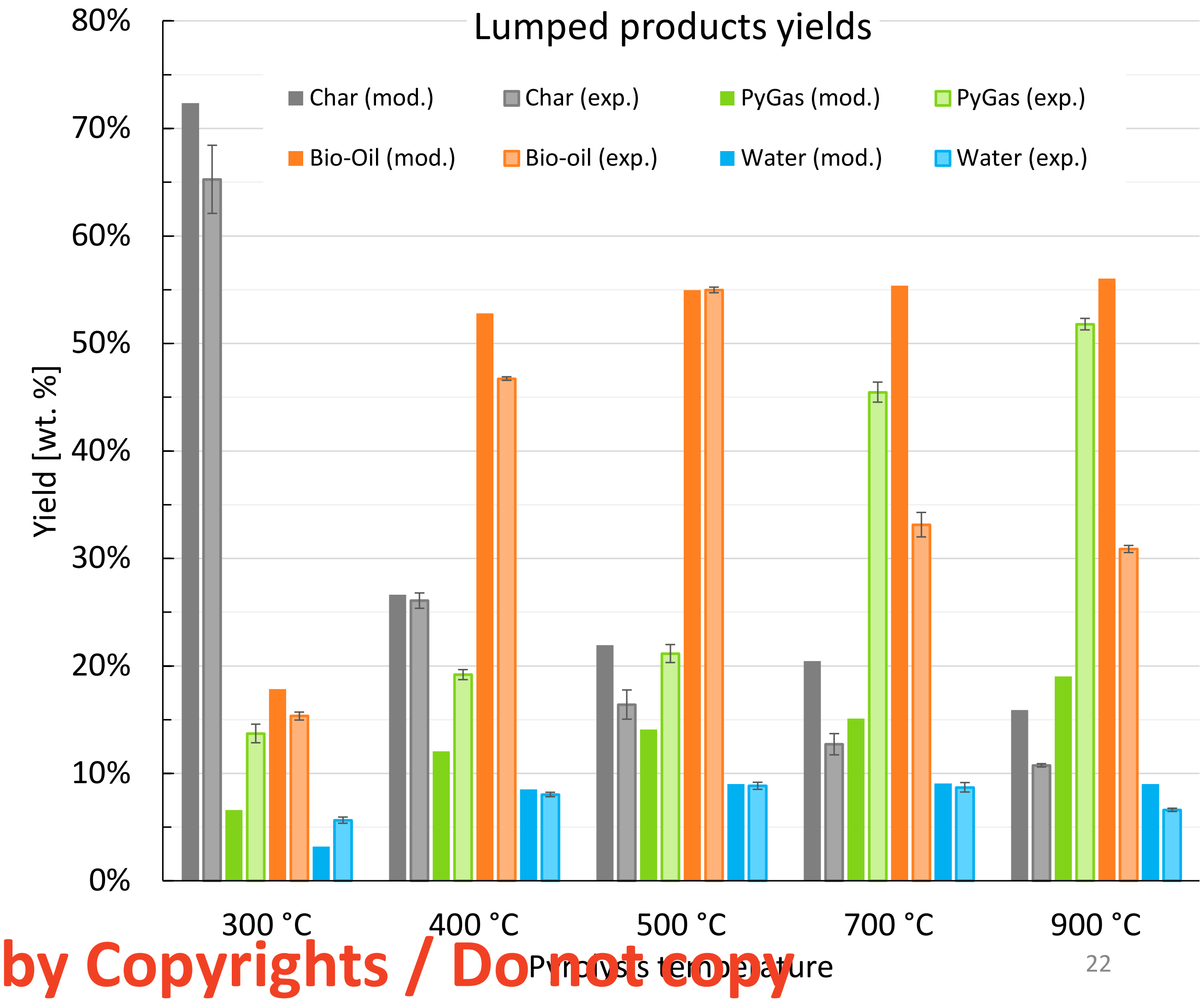
Model validation – mass loss profile fit

- Mass loss profiles has worse fit then center temperature profile
- That indicate discrepancy in the model that needs to be improved
- For 300 °C the model does not show a good fit
- For 400 °C and 500 °C the show moderate fir, but a antifactory precise char yield
- For the 700 °C and 900 °C model show good fir in the initial stage, but in the end overpredicts the char yield



Model validation – yields of lumped products

- Up to 500 °C the model fairly well predicts the yields of the lumped products (char, bio-oil, pygas and water)
- Up to 500 °C model underestimate pygas yield in exchange for char and bio-oil
- Above 500 °C the secondary gas phase reactions (cracking) become relevant, which model do not cover
- Above 500 °C model overpredicts bio-oil and char yield in expense of the pygas yield



Model validation – improvements to implementation

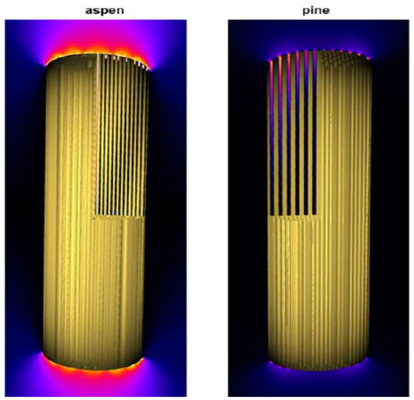
- **Secondary reactions in the gas phase**
  - particle's surrounding have to modeled

- **Validation of the results of the model with the GC/MS-FID bio-oil composition**
  - invalidation of the secondary gas phase reactions accuracy

- **Particle shrinking** - not possible to easily implement in the currently used software, although exp. data available

- **Implementation of the true density and porosity change, and the wood-dedicated thermal conductivity model** - data available, but shrinking have to be implemented first

Release of the vapours to the surrounding

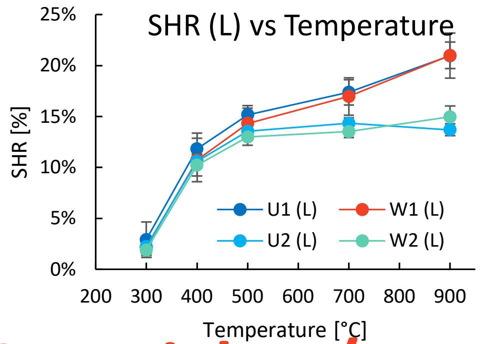


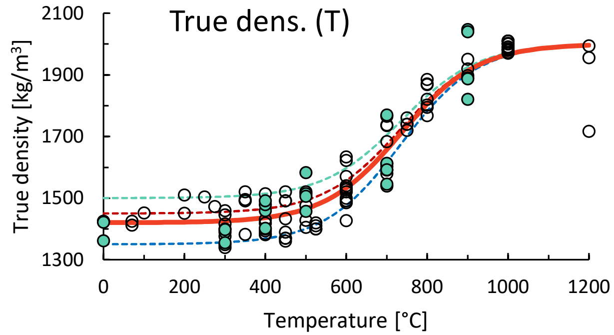
(Ciesielski et al. 2020)

Secondary cracking reactions in the gas phase in temperatures above 500 °C

			Reaction	Δh [kJ/g]
1	HAA/AA	→	$1.5\,H_2 + 1.5\,CO + 0.25\,CO_2 + 0.25\,CH_4$	0.411
2	GLYOX	→	$H_2 + 2\,CO$	−0.160
3	C_3H_6O	→	$0.5\,CO_2 + C_2H_4 + 0.5\,CH_4$	0.583
4	$C_3H_4O_2$	→	$CO_2 + C_2H_4$	−0.915
5	HMFU	→	$3\,CO + 1.5C_2H_4$	0.642
6	pCOUMARYL	→	$2\,CO + 1.5C_2H_4 + CH_4 + 3C$	−0.060
7	PHENOL	→	$CO + C_2H_4 + 0.5\,CH_4 + 2.5C$	0.095
8	FE2MACR	→	$4\,CO + C_2H_4 + 2\,CH_4 + 3C$	−0.261
9	CH_2O	→	$H_2 + CO$	0.180
10	CH_3OH	→	$1.5\,H_2 + 0.5\,CO + 0.25\,CO_2 + 0.25\,CH_4$	0.905
11	CH_3CHO	→	$CO + CH_4$	−0.441
12	ETOH	→	$H_2 + CO + CH_4$	1.091
13	HCOOH	→	$H_2 + CO_2$	−0.324

(Anca-Couce et al. 2017)





Summary

- Established model valid for board range of particle size and temperature (> 500 °C)
- Experimental data with low standard deviation – broad dataset
- Satisfactorily good fit of the model to the experimental data
- Model still needs to be slightly adjusted to obtain required accuracy and precision
- **Expanded model should be able to predict the changes in the pore structure of char**

Future read

Review of the properties of the wood and its char
Summary of the parameters and auxiliary functions

Production of Biofuels and Chemicals with Pyrolysis pp 373-438 | Cite as

Review on Modelling Approaches Based on Computational Fluid Dynamics for Biomass Pyrolysis Systems

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Changes in the structure during pyrolysis
Foundation for the model expansion with the structure changes

ELSEVIER
Applied Energy
Volume 286, 15 March 2021, 116431

Tailoring of the pore structures of wood pyrolysis chars for potential use in energy storage applications

Przemyslaw Maziarka [a], Peter Sommersacher [b], Xia Wang [c], Norbert Kienzl [b], Stefan Retschitzegger [b], Wolter Prins [a], Niklas Hedin [c], Frederik Ronsse [a]

https://doi.org/10.1016/j.apenergy.2020.116431

ELSEVIER
Chemical Engineering Journal
Available online 4 March 2021, 129234
In Press, Journal Pre-proof

Do you BET on routine? The reliability of N_2 physisorption for the quantitative assessment of biochar's surface area

Przemyslaw Maziarka [a, 1], Christian Wurzer [b, 1], Pablo J. Arauzo [c], Alba Dieguez-Alonso [d], Ondřej Mašek [b], Frederik Ronsse [a]

https://doi.org/10.1016/j.cej.2021.129234

Metanalysis of sub-models for single particle pyrolysis of wood Practical information regarding establishing a model

Working title

Thermo-physical and chemical aspects in the pyrolysis of the single particle of wood in thermally thick regime: metanalysis in practice

Publication in preparation

Thank you for your attention!

Detailed questions?

-> Przemyslaw Maziarka

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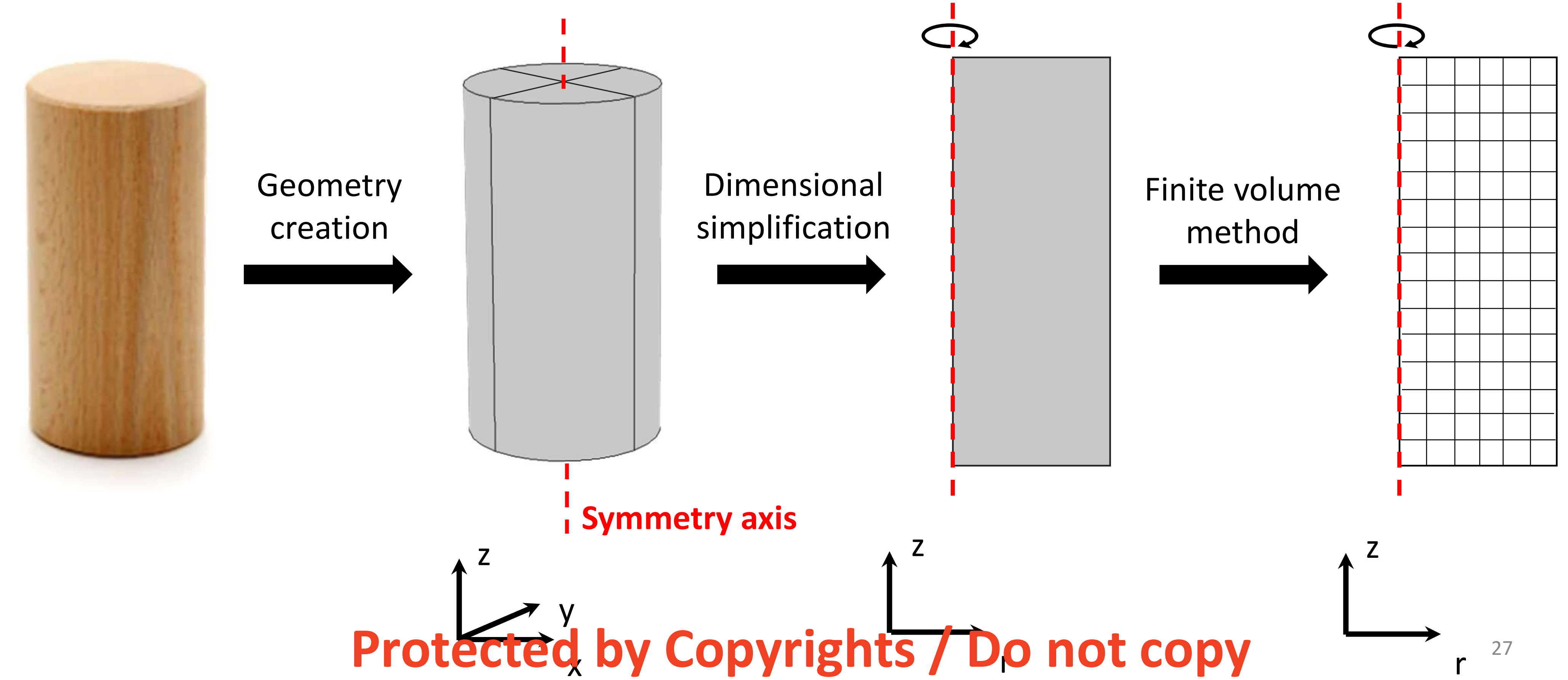
Model in brief – domain, dimensions and mesh

Wooden cylinder real domain | **Model 3D** representation | **Model 2D-axi** representation | **Meshed domain** comput. framework



Model in brief – governing equations and boundary cond.

Mass

Solids

G: $$\frac{\partial}{\partial t} < \rho_{i,s} >= \dot{\omega}_{i,s}$$

B: $$D_{eff}\nabla(< \rho_s >)\,|_{x=x_B} = 0$$

Fluid

G: $$\frac{\partial}{\partial t} < \rho_i > + \nabla < u_G \rho_i >= \dot{\omega}_i$$

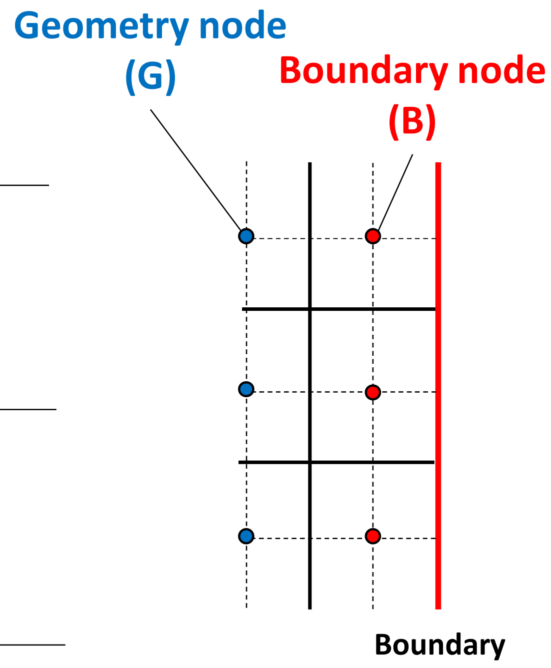
B: $$D_{eff}\nabla(< \rho_i >^G)\,|_{x=x_B} = h_m[\,\rho_{i,\infty} - < \rho_i >^G |_{x=x_B}]$$

Flow

Fluid

G: $$< u_G >= \frac{K_{G,eff}}{\mu_G}\nabla(< P_G >)$$

B: $$< P_G >\,|_{x=x_B} = P_\infty$$



Energy

G: Accumulation / Convection / Conduction / Reaction

$$\frac{\partial T}{\partial t}(< \rho_S > C_{P,S} + \varepsilon_G < \rho_G >^G C_{P,G}) + \nabla T\left(\varepsilon_G \sum_{i=1}^{N} < u_i \rho_i > C_{P,i}\right) = \nabla(\lambda_{eff}\nabla T) + Q$$

B: Conduction / Convection / Radiation

$$\nabla(\lambda_{eff}\nabla T)\,|_{x=x_B} = h_T(T_{flow,\infty} - T\,|_{x=x_B}) + \sigma\omega(T_{wall}^4 - T^4|_{x=x_B})$$