Development of a Detailed Approach to Model the Solid Pyrolysis with the Coupling Between Solid and Gases Intra-pores Phenomena

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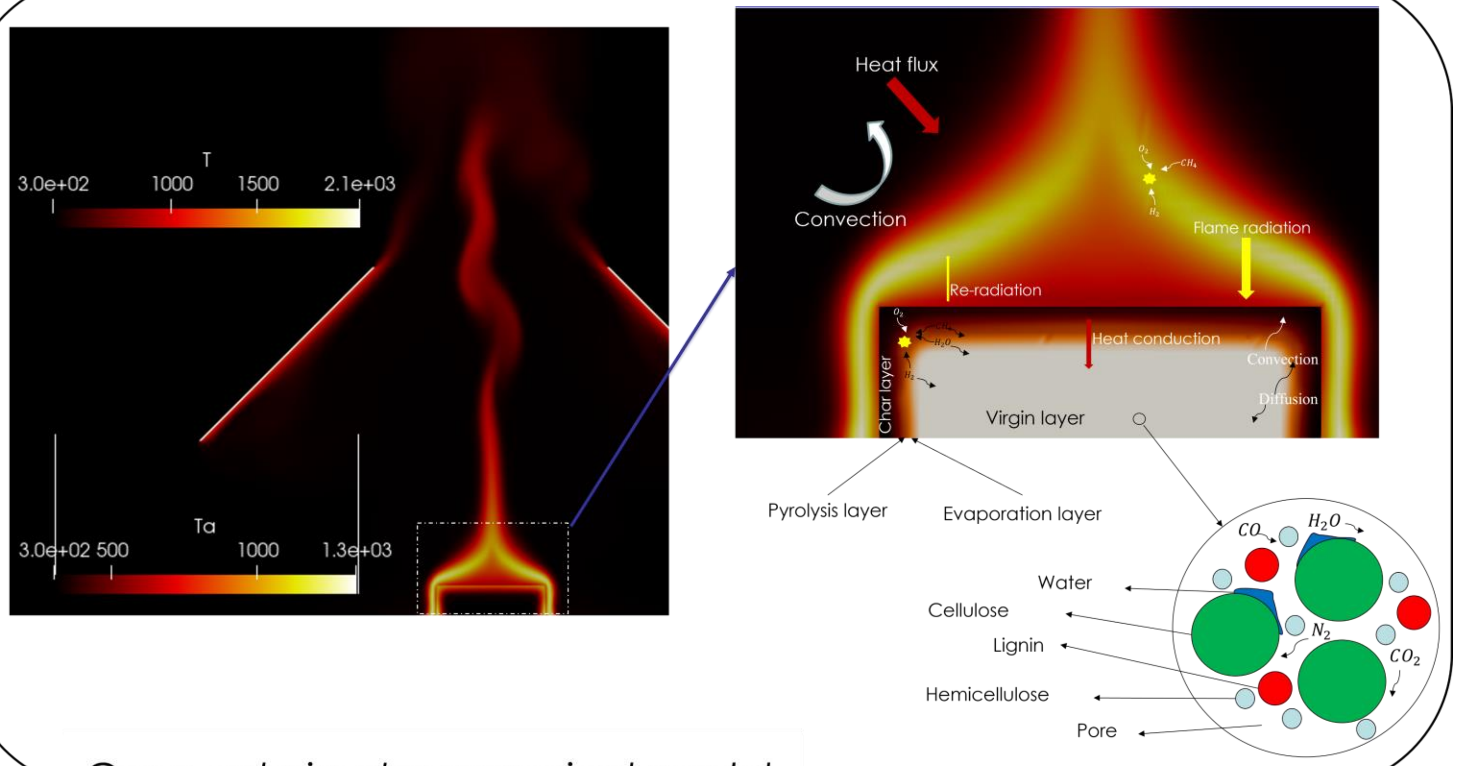


Cone calorimeter numerical model

Introduction

- **Wood pyrolysis:**
  - A thermo-chemical decomposition process at high temperatures in the absence of oxygen.
  - Having applications in many fields: fire safety, bioenergy …

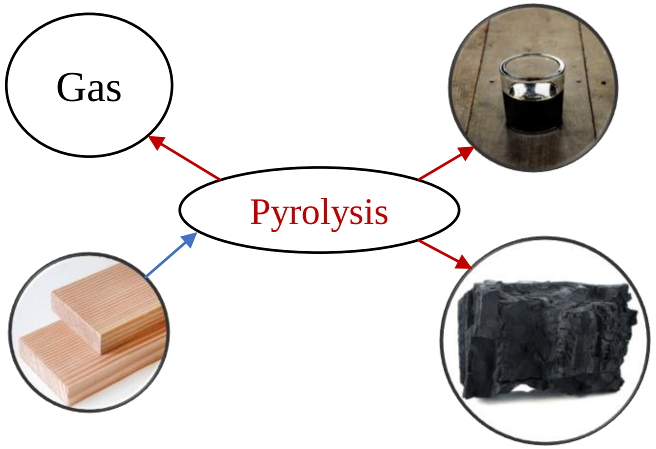
Fire in Sequoia National Forest in California (Sept 2021)

Wood bio-energy

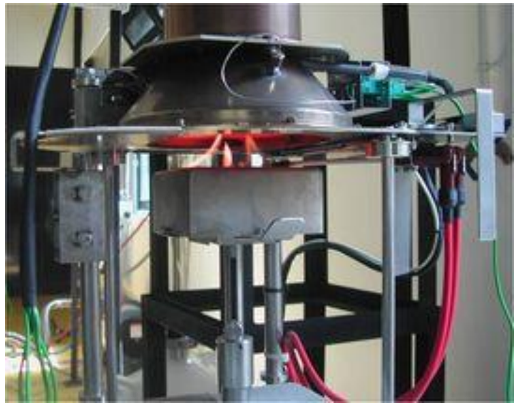
Fire of wooden house

Introduction

- **Current State of Knowledge and Techniques**:



Thermogravimetric Analysis (TGA)



Cone Calorimetry

- **Limitations:**

Oversimplify the pyrolysis process and neglect some important aspects

Capture more accurately behaviour →

Model with complex mechanisms, the complex interactions between the solid and gas phases within the wood's porous structure during pyrolysis

- Only focus on initial and final components, ignore intermediate phase
- The pyrolysis process is not infinitely fast
- Ignore interaction between solid and gases intra-pores phenomena in **porous material**

- « Detailed reactions » for solid part
- Modelise the wood as the porous material

- **TGA Scale Model**

k

Reaction i

$CH_4, CO, CO_2, \ldots$

t

$\pi_i = (1-\gamma_i)\partial\rho_{k,i}$

Conversion: $\alpha_i = \frac{\rho_k(t=0)-\rho_k(t)}{\rho_k(t=0)-\rho_k(t=\infty)}$

$\frac{d\alpha_i}{dt} = k_i\, f(\alpha_i)$

Kinetic rate: $k = A.e^{-\frac{Ea}{R.T}}$

« Reaction model »
$f(\alpha_i) = (1-\alpha_i)^{n_i}$

t

Conversion: $\alpha_i = \frac{\rho_{k,max}-\rho_k(t)}{\rho_{k,max}-\rho_k(t=\infty)}$

$\rho_1(t=0) = 0$
$\rho_1(t=\infty) = 0$

$\rho_{1,max} = \rho_0\gamma_0$

$$S_0 \xrightarrow{k_0} \gamma_0 S_1 + (1-\gamma_0)Gas$$

$$\xrightarrow{k_1} \gamma_1 S_2 + (1-\gamma_2)Gas \xrightarrow{k_3} \gamma_3 S_4 + (1-\gamma_3)Gas$$

$$\xrightarrow{k_2} \gamma_2 S_3 + (1-\gamma_2)Gas$$

Example of multiple-step mechanism

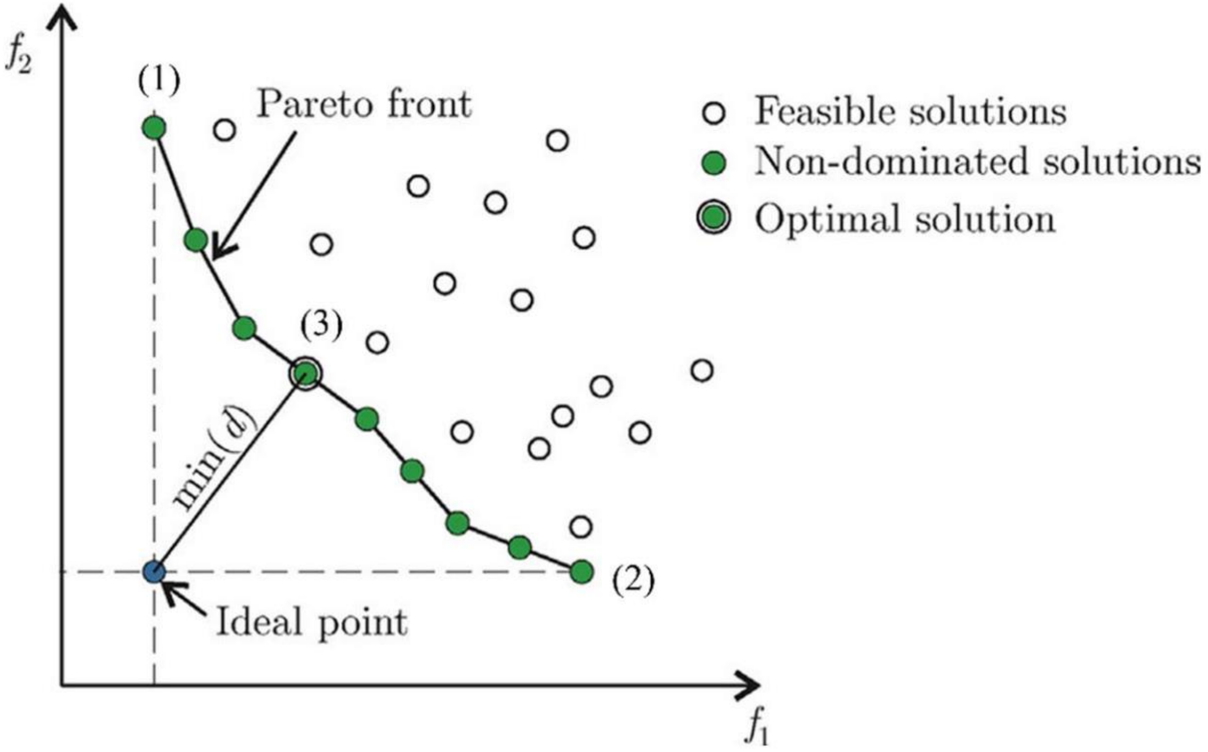
Methodology

➢ TGA Scale Model

❖ Optimization:

- Method: Multi-objective Genetic Algorithm (MOGA)
- Input variables for each reaction: A, E, γ, n
- Objective function:

$$\phi = \sqrt{\sum_{j}^{n_i}\left(\frac{\beta_1\left|m_{ex,j}-m_{nu,j}\right|}{n_i}+\frac{\beta_2\left|\frac{\dot{m}_{ex,j}}{\dot{m}_{ex,max}}-\frac{\dot{m}_{nu,j}}{\dot{m}_{ex,max}}\right|}{n_i}\right)^2}$$



Pareto front of MOGA

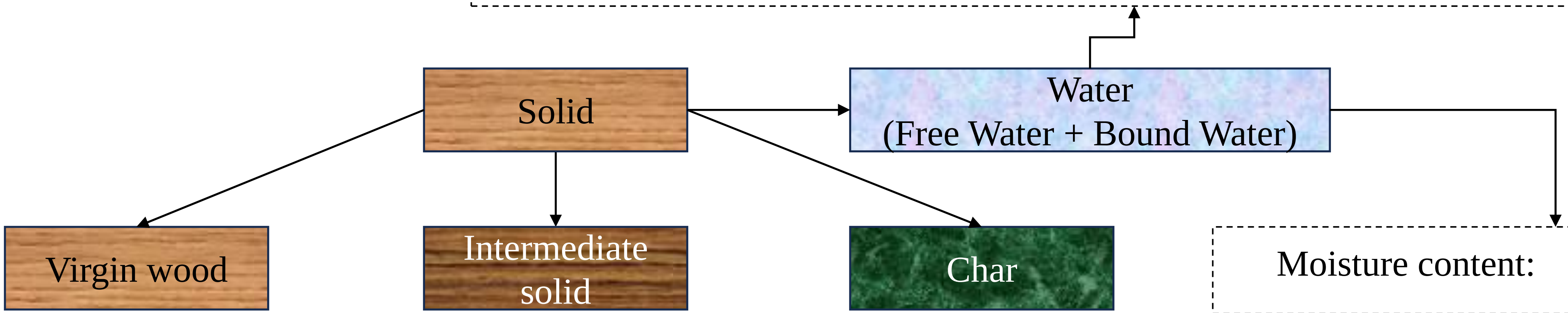
Methodology

➢ Cone Calorimetry Scale Model (PATO)

The Governing Equations	
Mass Conservation Equation	$\frac{\partial \epsilon_g \rho_g}{\partial t} + \underbrace{\nabla \cdot (\epsilon_g \rho_g v_g)}_{convection} = \underbrace{\pi_{tot}}_{pyrolysis\ gas\ rate}$
Momentum Conservation Equation	$v_g = -\frac{1}{\epsilon_g}\frac{K}{\mu_g}\nabla p_g$ (Darcy's law)
Energy Conservation Equation	$\underbrace{\frac{\partial(\epsilon_g \rho_g h_{g,s})}{\partial t} + \frac{\partial(\epsilon_g \rho_g h_{g,c})}{\partial t} - \frac{\partial(\epsilon_g p_g)}{\partial t}}_{gaseous\ energy\ storage} + \underbrace{\frac{\partial(\rho_s h_{s,s})}{\partial t}}_{solid\ energy\ storage} + \underbrace{\nabla \cdot (\epsilon_g h_{g,s} v_g)}_{convection} = \underbrace{\nabla \cdot (k \nabla T)}_{conduction} + \underbrace{\sum h_{p,i}\pi_{Ri}}_{pyrolysis\ energy\ flux} + \underbrace{\nabla q_{rad}}_{radiation\ term}$
Species Conservation Equation	$\frac{\partial(\epsilon_g \rho_g Y_i)}{\partial t} + \underbrace{\nabla \cdot (\epsilon_g \rho_g Y_i v_g)}_{convection} = \underbrace{\nabla \cdot \left(\rho_g \frac{D_{Y,eff}}{\eta} \nabla Y_i\right)}_{diffusion} + \underbrace{\pi_i}_{pyrolysis\ gas\ rate} + \underbrace{\dot{\omega}_i}_{gas\ homogenious\ reaction}$

Methodology

➢ Cone Calorimetry Scale Model



Mass of water:

$$\frac{\partial \rho_{water}}{\partial t} - \underbrace{\frac{\rho_{water} K}{\mu_{water}} \Delta p}_{\substack{Convection,\\ only\ for\ free\ water}} = \underbrace{-k_{water}\left(\frac{\rho_{water}}{\rho_{water,init}}\right)^{n} \rho_{water,init}}_{Evaporation}$$

Moisture content:

$$M = \frac{\rho_{s,init}}{\rho_{s,init} - \rho_{water}}$$

❖ Solid properties:

- Thermo conductivity, Heat capacity = $f(M, phase\ mass\ fraction)$
- Porosity, Permeability = $f(M, phase\ volume\ fraction)$

Gas properties are calculated through Cantera

Results and Analysis

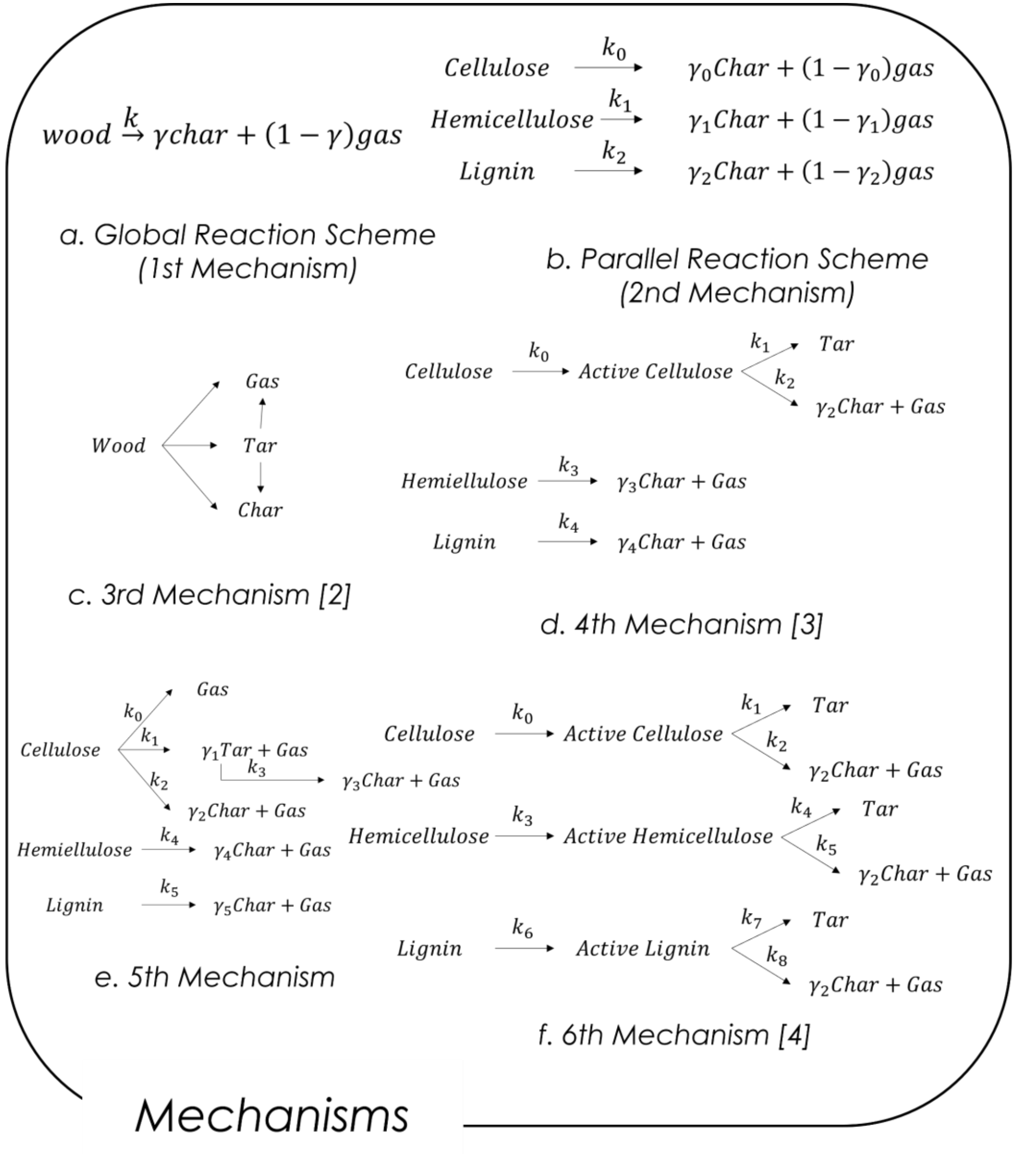
➢ TGA Scale

Proportion of component in Douglas fir [1]

Component	Density (kg/m^3)
Cellulose	181.95
Hemicellulose	117
Lignin	121.35

Controlled temperature:

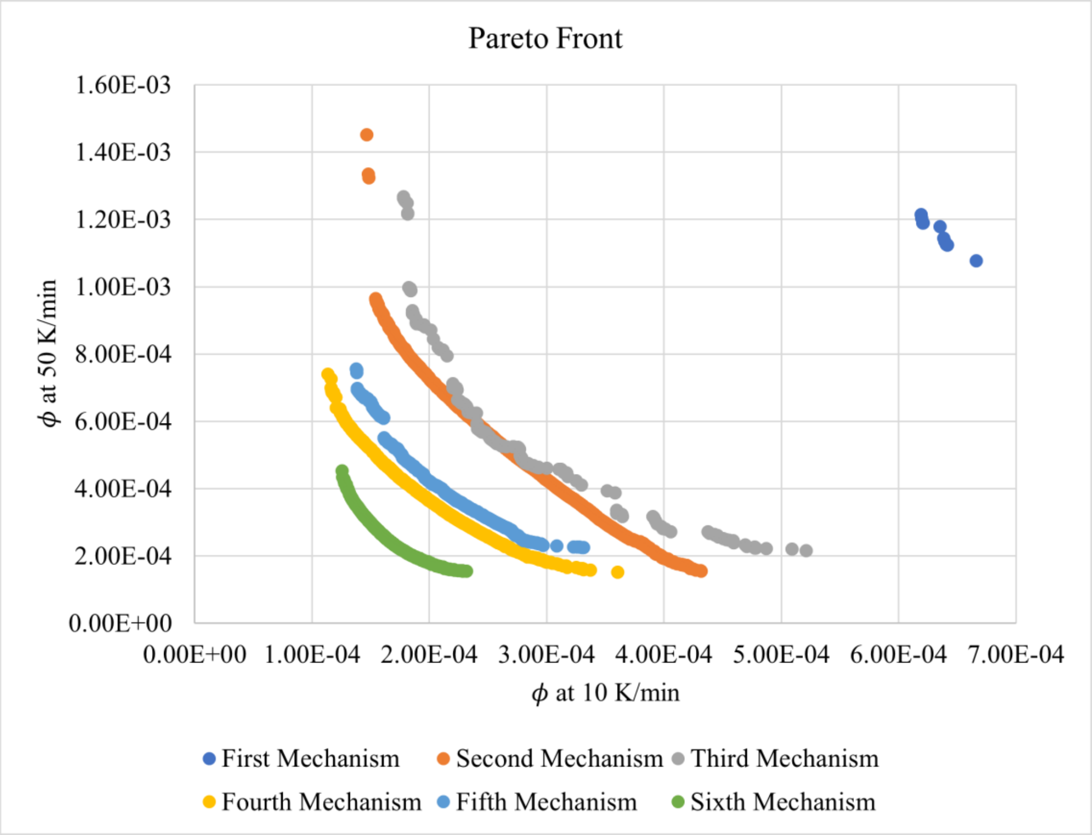
- ❖ Range of temperature: 303.15 K -1173.15 K
- ❖ Heating rate: 10 K/min, 50 K/min



[1] Morten Gunnar Grønli, “*A theoretical and experimental study of the thermal degradation of biomass*”
[2] Shafizadeh, Fred and Chin, Peter PS, "*Thermal deterioration of wood*“
[3] Shafizadeh, Fred, "*Introduction to pyrolysis of biomass*“
[4] Koufopanos, CA and Lucchesi, A and Maschio, G, "*Kinetic modelling of the pyrolysis of biomass and biomass components*"

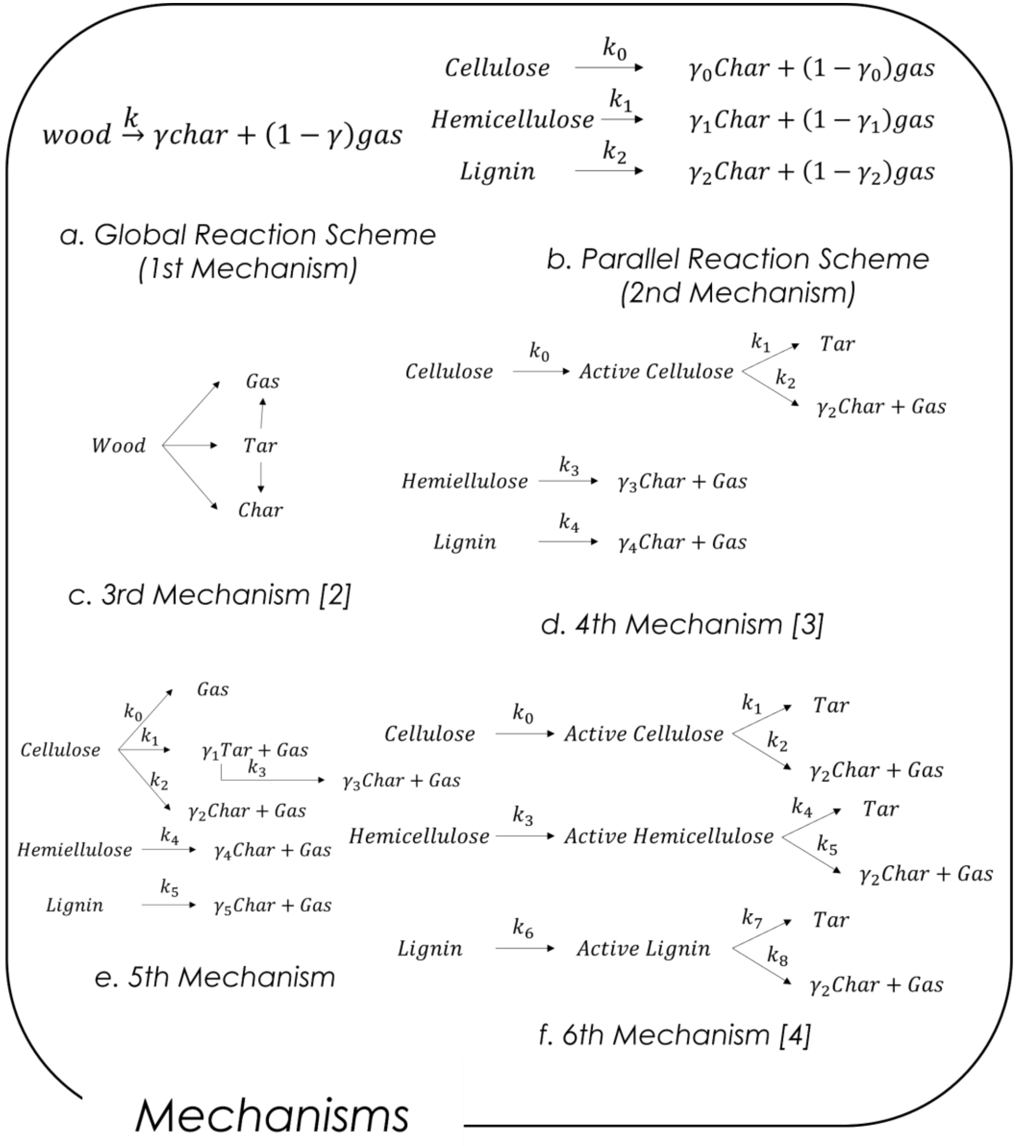
Results and Analysis

➢ TGA Scale



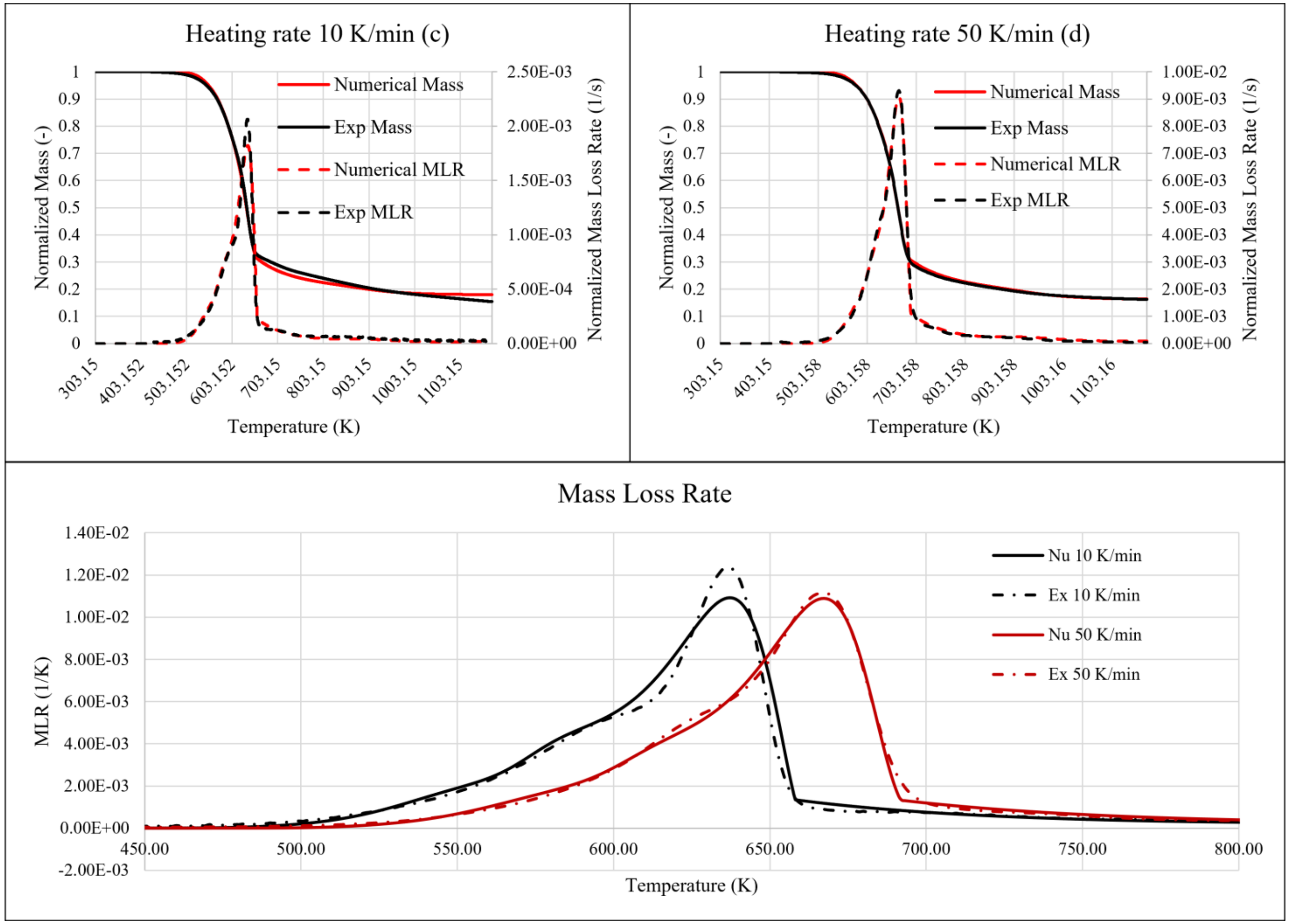
❖ Multiple initial-component mechanisms return better results than single initial-component mechanisms.

❖ Multiple-step mechanisms fit experiment more than single-step mechanism



Results and Analysis

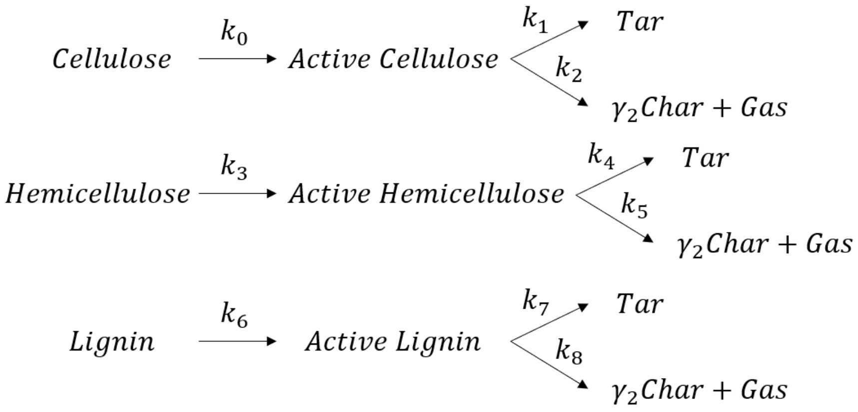
- **Optimal results for 6th mechanism**



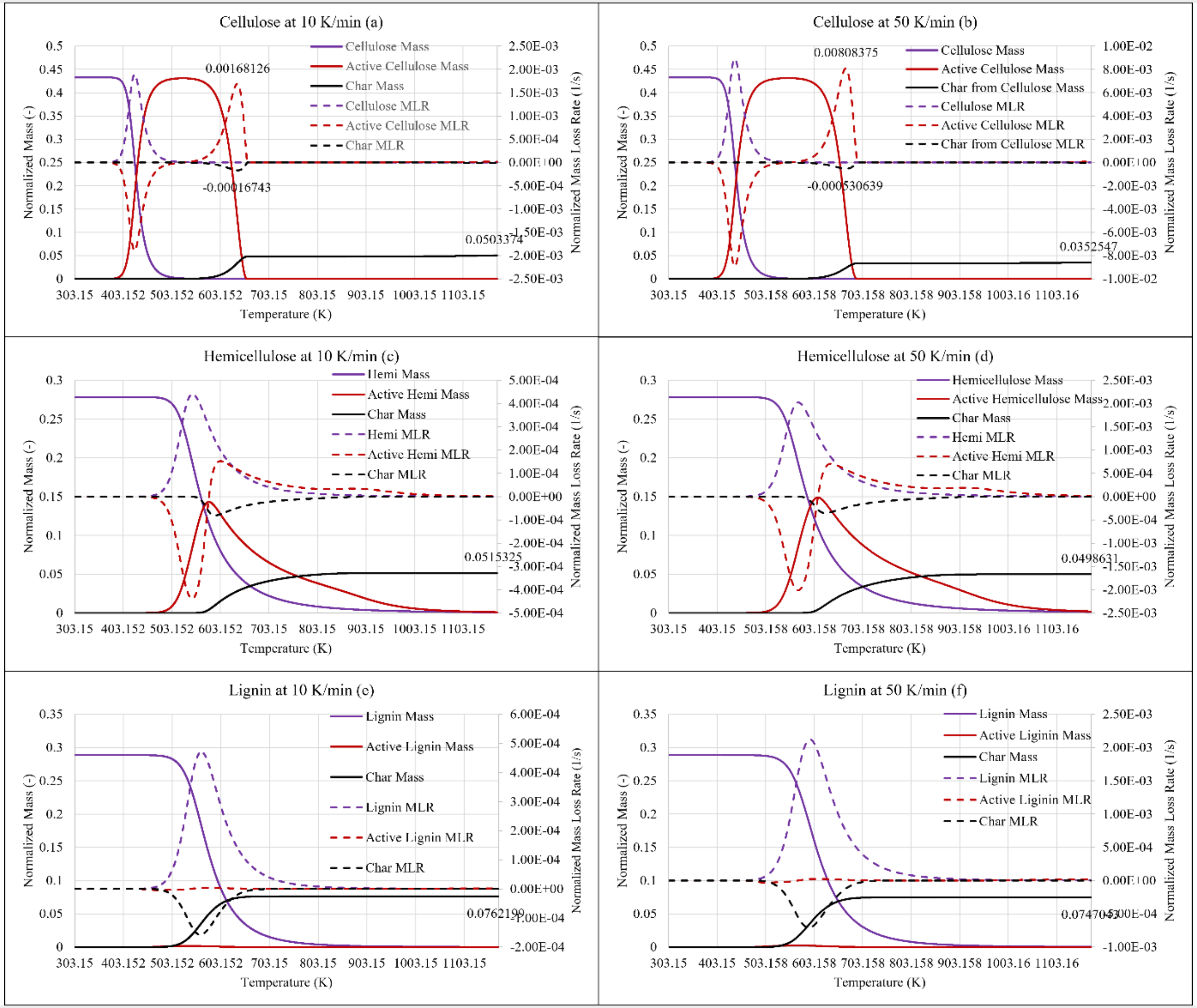
- With optimal kinetic parameters, simulation can capture well the evolution of both mass and mass loss rate in experimental test.

Results and Analysis

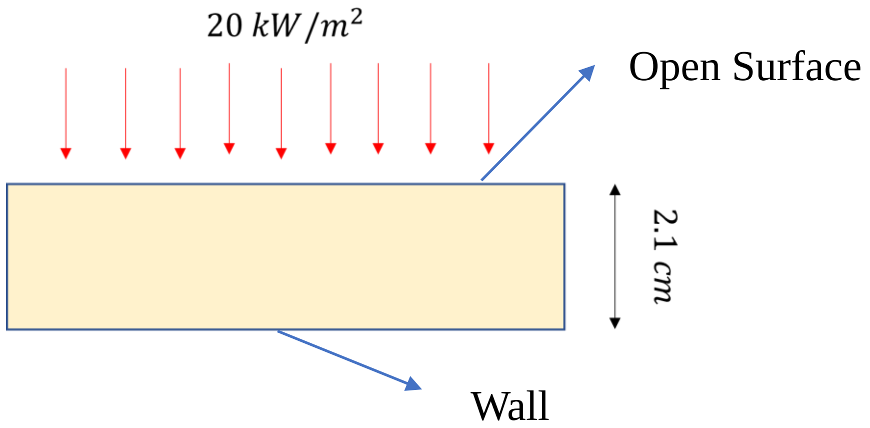
- **Optimal results for 6th mechanism**



The mass of char producted by each component is different at 2 heating rate → Expected properties of competitive mechanism.



Cone Scale



1D model

$$Cellulose \xrightarrow{k_0} Active\ Cellulose \begin{cases} \xrightarrow{k_1} Tar \\ \xrightarrow{k_2} \gamma_2 Char + Gas \end{cases}$$

$$Hemiellulose \xrightarrow{k_3} \gamma_3 Char + Gas$$

$$Lignin \xrightarrow{k_4} \gamma_4 Char + Gas$$

Applied mechanism

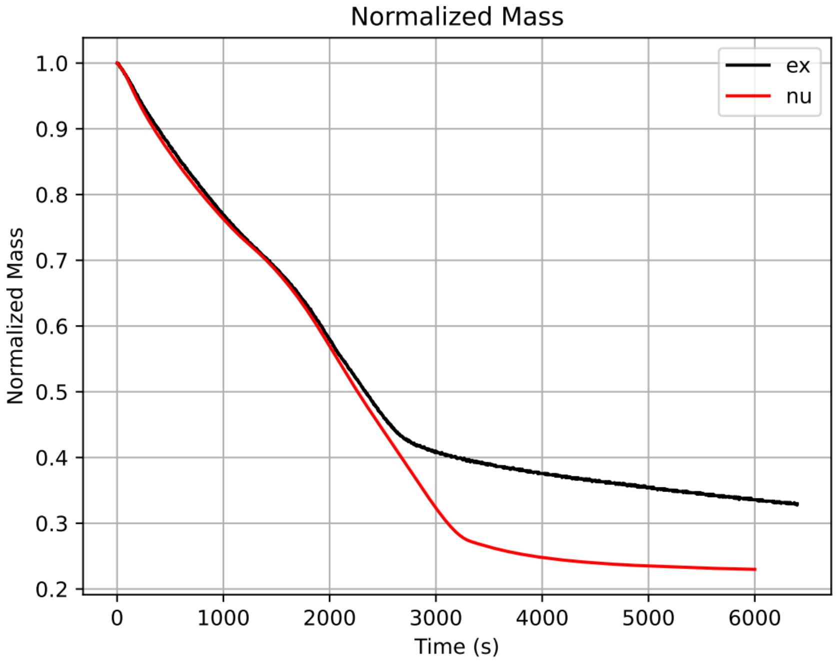
Sample	Mass fraction of pyrolysis gas [1]					
	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6
Cellulose	0.02764	0.23748	0.67547	0.03967	0.00221	0.01753
Hemicellulose	0.01783	0.45138	0.47096	0.04789	0.00364	0.0083
Lignin	0.0596	0.33873	0.49139	0.09106	0.0012	0.01802

**Assumption: Types of producted gas in all pyrolysis process are in the same proportion with each initial component*

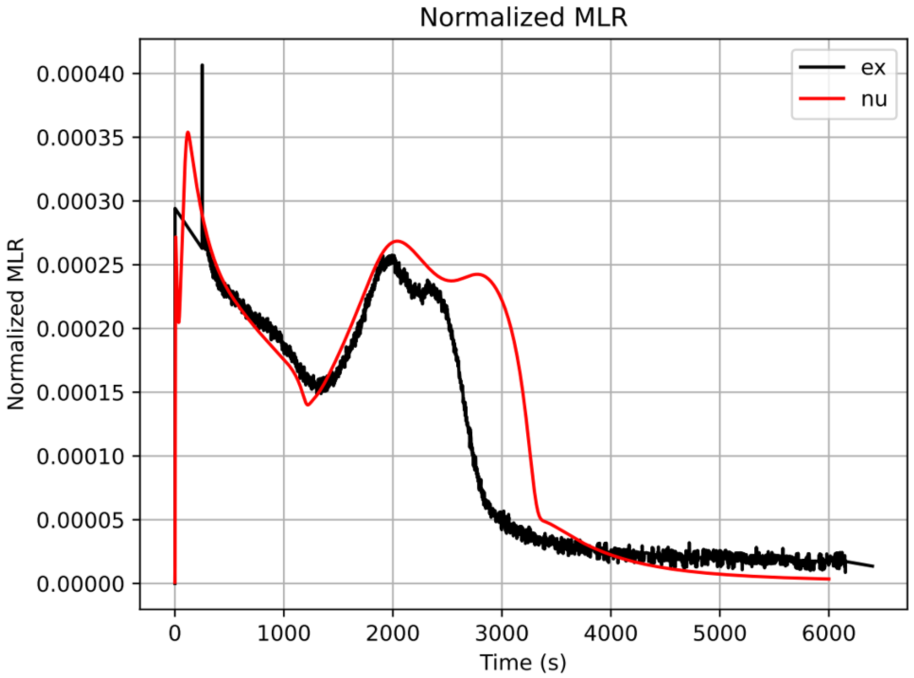
[1] Park, Won Chan and Atreya, Arvind and Baum, Howard R, "*Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis*"

Results and Analysis

➢ **Cone Scale**



Mass evolution



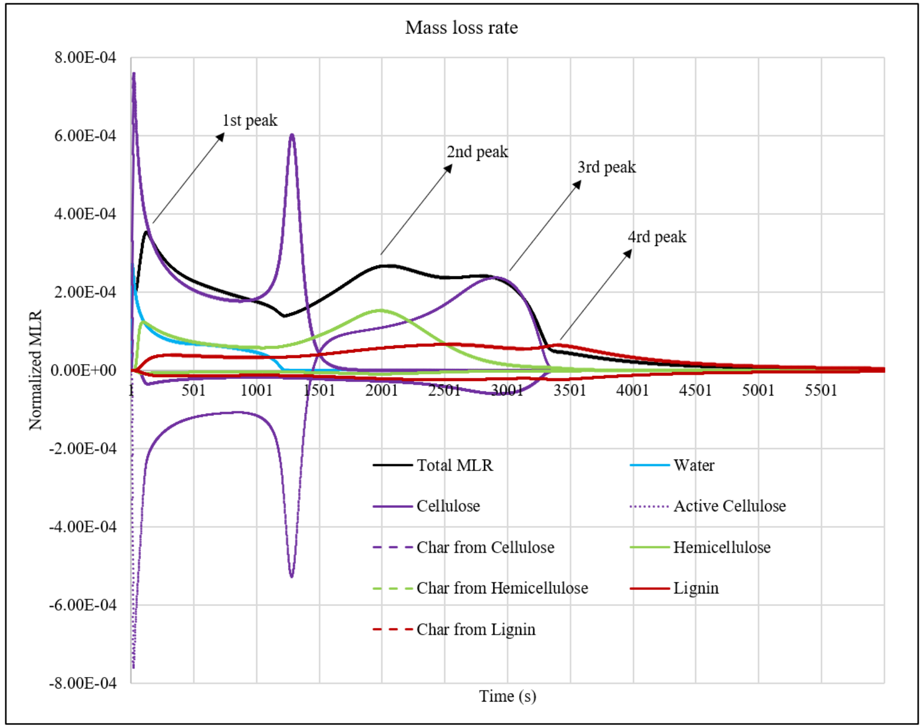
Mass loss rate evolution

❖ Before first 2000s, mass evolution captures the experiment perfectly. However, a significant difference appears in final mass between simulation and experiment.

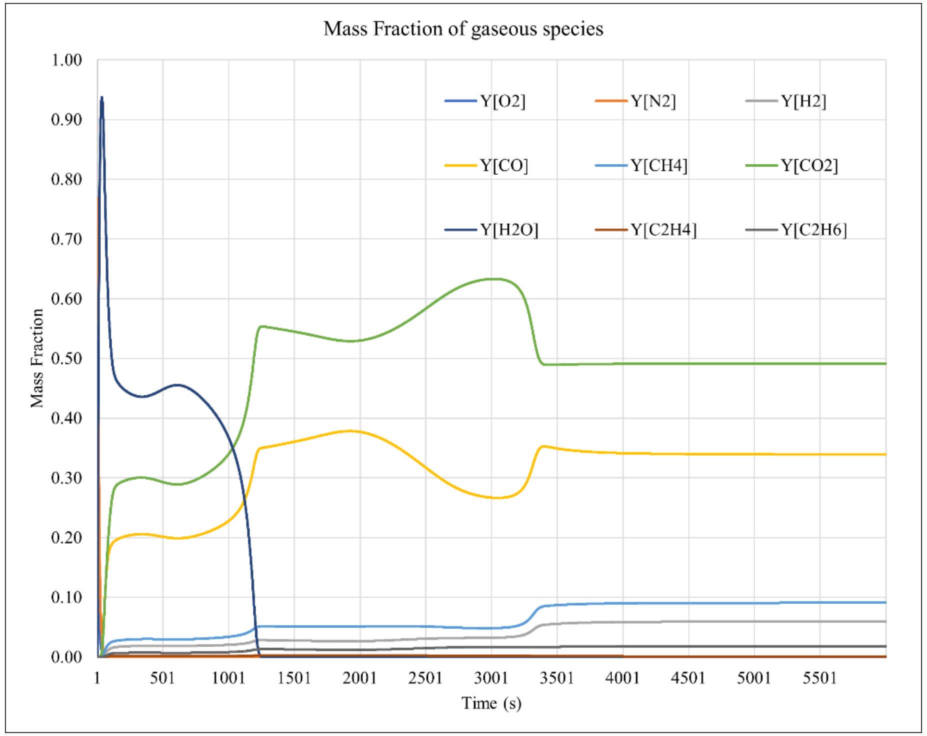
❖ MLR plot describes well the behaviour of experiment sample. But reaction time delays when compared to experiment.

Results and Analysis

➢ Cone Scale



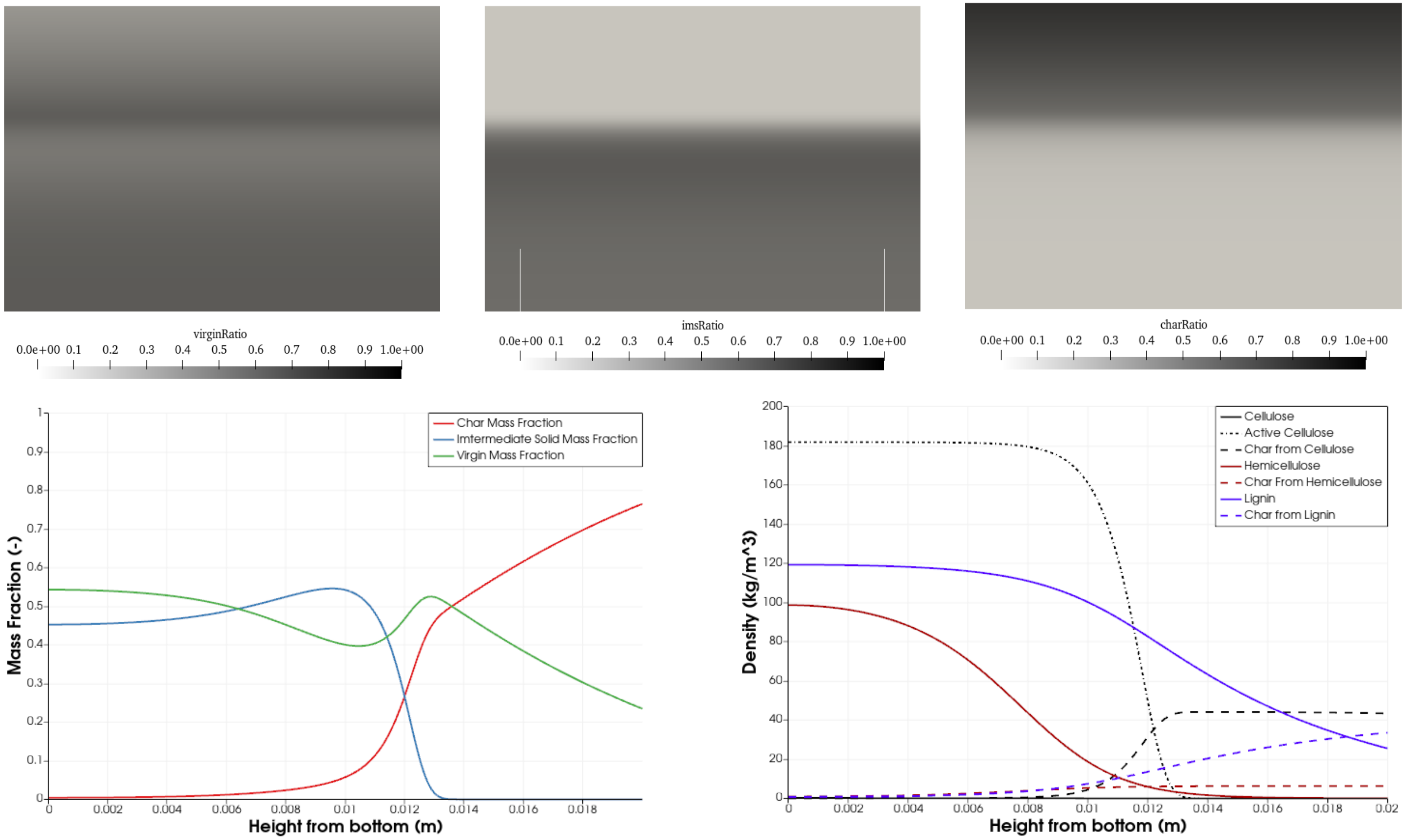
Average MLR of components



Average mass fraction of gaseous species

- ❖ Behaviour of each component is right to literature.
- ❖ Proportion of gaseous species strongly depends on pyrolysis process.

- **Cone Scale**



Solid Species Distribution (at 2000s)

Conclusion

- **TGA Scale:**
  - Having comparison among mechanisms.
  - Optimal parameters captures well the experimental test.

- **Cone Calorimetry Scale:**
  - Being able to apply competitive mechanisms.
  - Being able to capture the behavior of wood under thermo stress.
  - Considering the effect of gaseous phase.
  - Still having the difference in final mass.

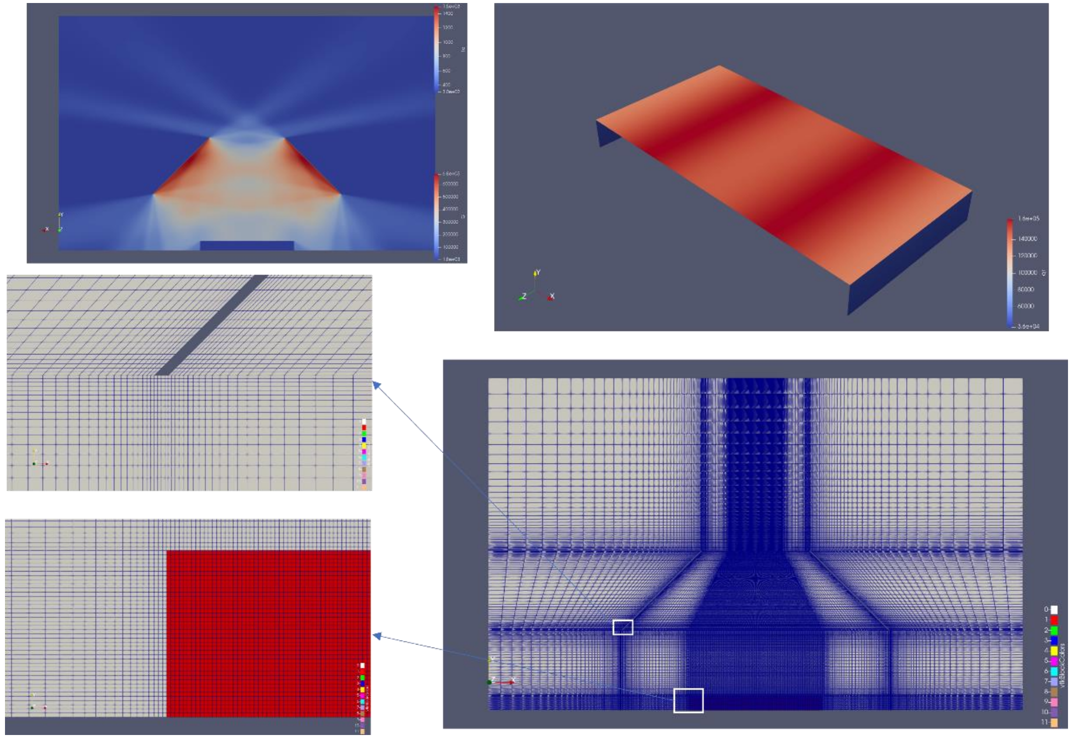
Future Work and Perspective

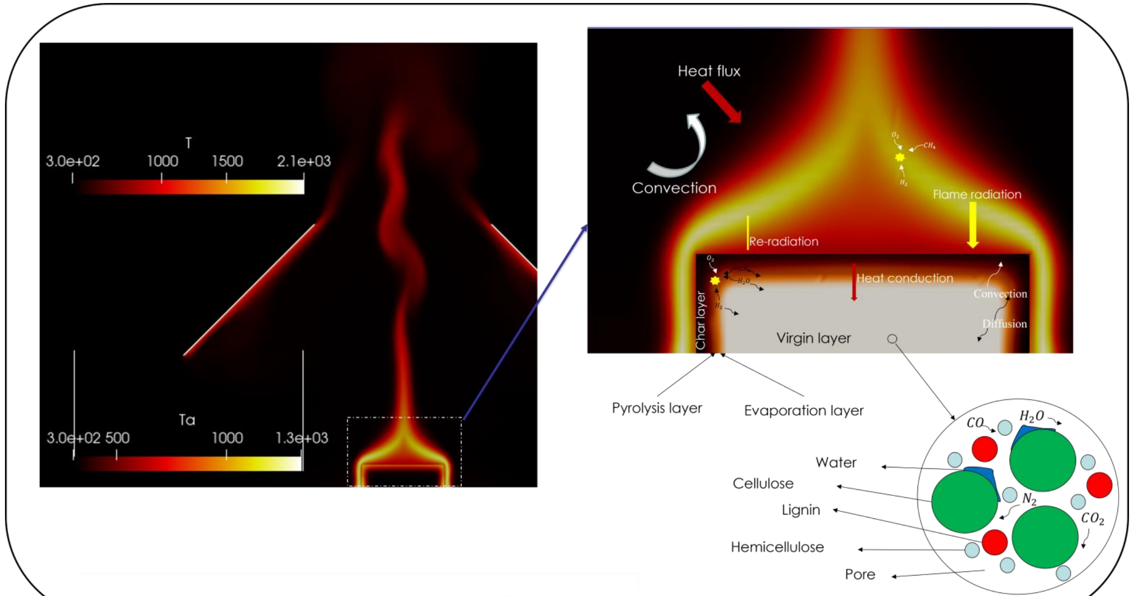
- To solve the difference of final mass: A model taking into account the effect of type of gas is being developed:

$$n_{cone} = f(Y_C, n_{tga})$$

$$k_{cone} = f\left(Y_C, k_{tga}\right)$$

- Implement the surrounding atmosphere: A full model is already developed and in the testing.

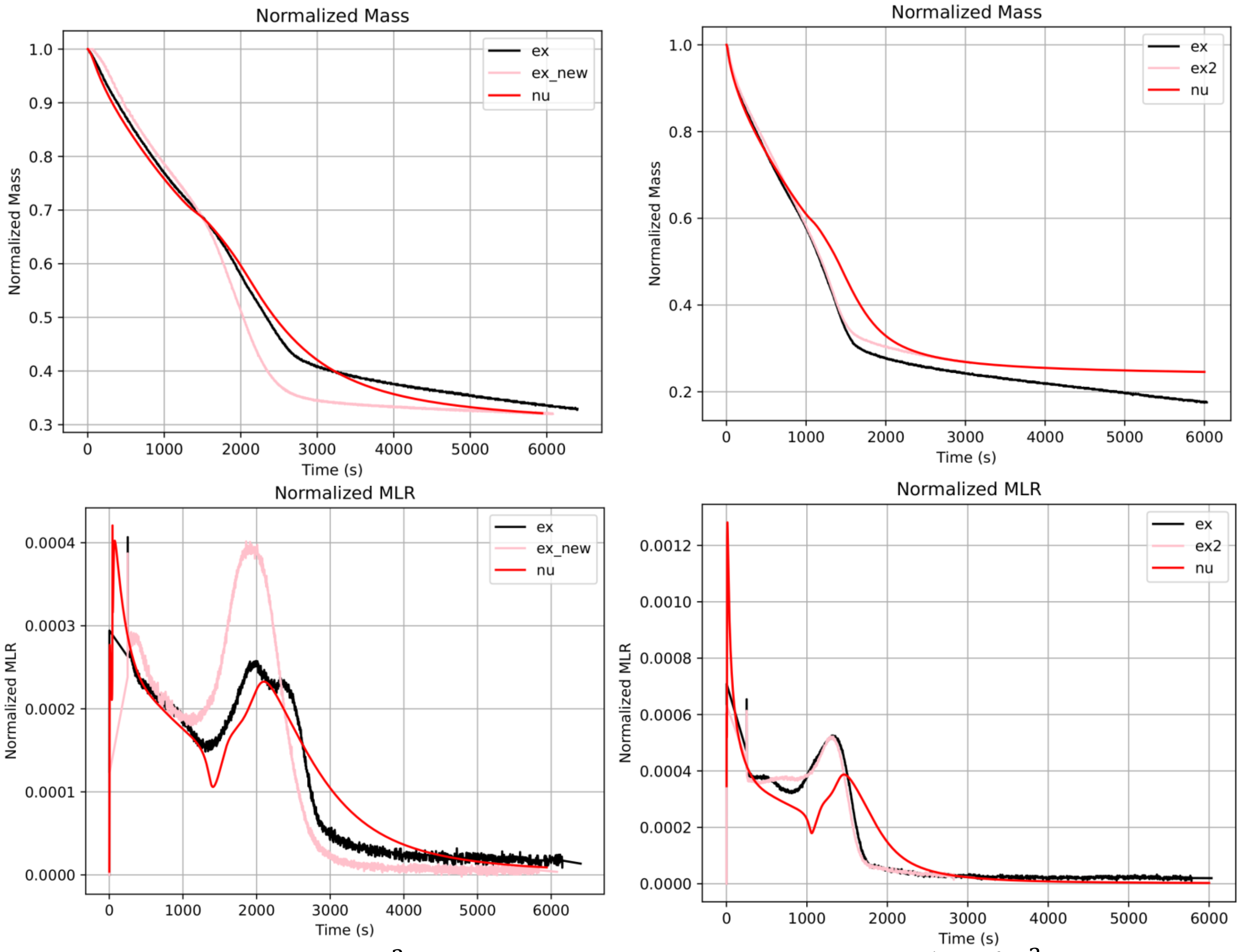




Cone calorimeter numerical model

Future Work and Perspective

- ❖ A model taking into account the effect of type of gas is being developed:
  $n_{cone} = f(Y_C, n_{tga}), k_{cone} = f(Y_C, k_{tga})$
- ✓ Be able to control the final mass, the evolution of mass loss rate



$20\ K/m^2$ $50\ K/m^2$

Thank You!!!

Questions???

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