

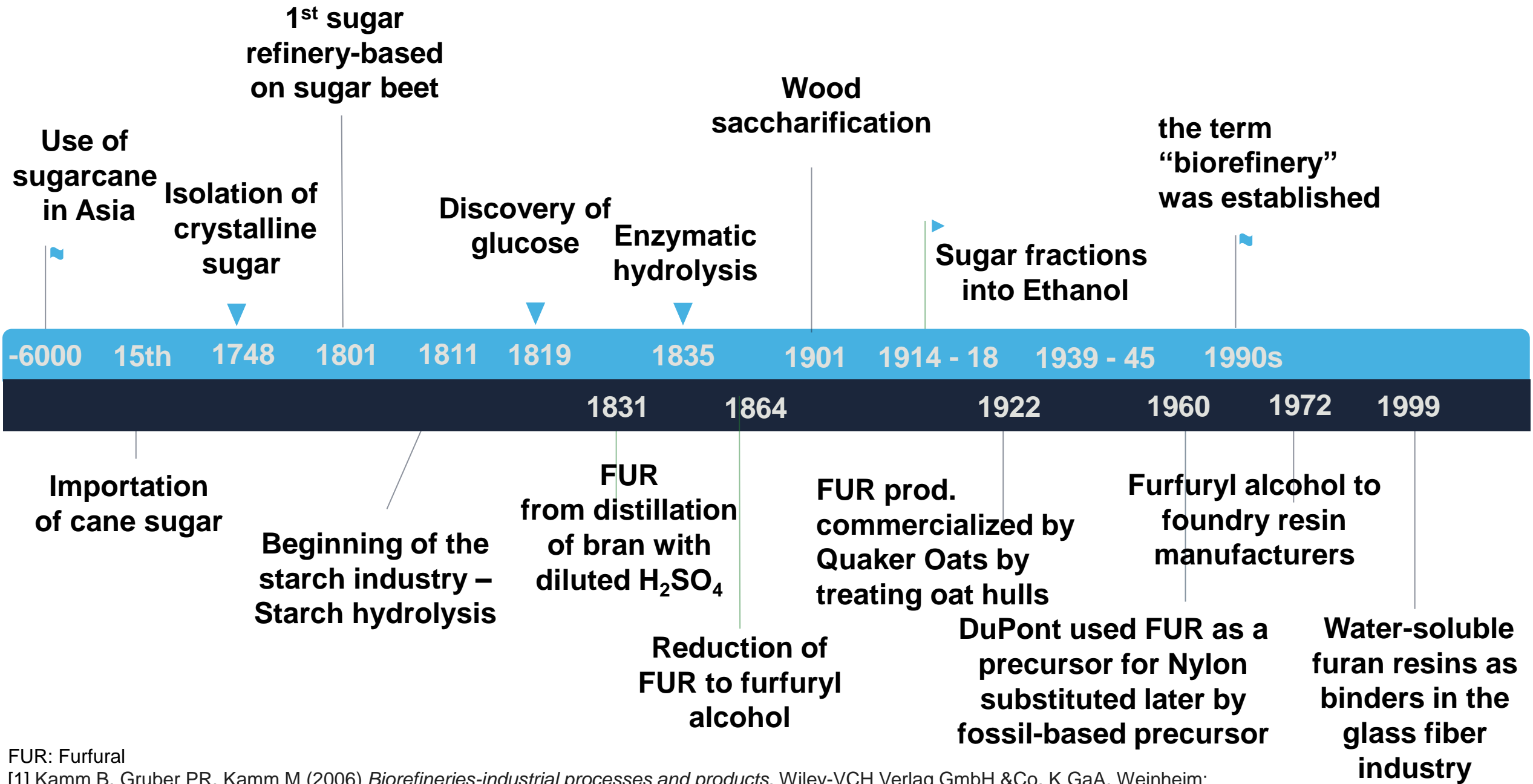


# Au coeur de la bioraffinerie thermochimique: les enjeux de la modélisation

Mercredi 15 mai 2024  
Par Marion Carrier



# Valorisation de la matière lignocellulosique de tout temps



FUR: Furfural

[1] Kamm B, Gruber PR, Kamm M (2006) *Biorefineries-industrial processes and products*. Wiley-VCH Verlag GmbH & Co. K GaA, Weinheim;

# Définitions

From the US Department of Energy :

Une **bioraffinerie** est un concept global d'usine de traitement où **les matières premières de la biomasse** sont **converties et extraites** en une **gamme de produits de valeur**.

From NREL:

Une bioraffinerie est une installation qui **intègre** des processus et des équipements de conversion de la biomasse pour produire des **carburants**, de l'**électricité** et des **produits chimiques** à partir de la biomasse. Le concept de bioraffinerie est **analogue aux raffineries de pétrole** actuelles, qui produisent de multiples carburants et produits à partir du pétrole.

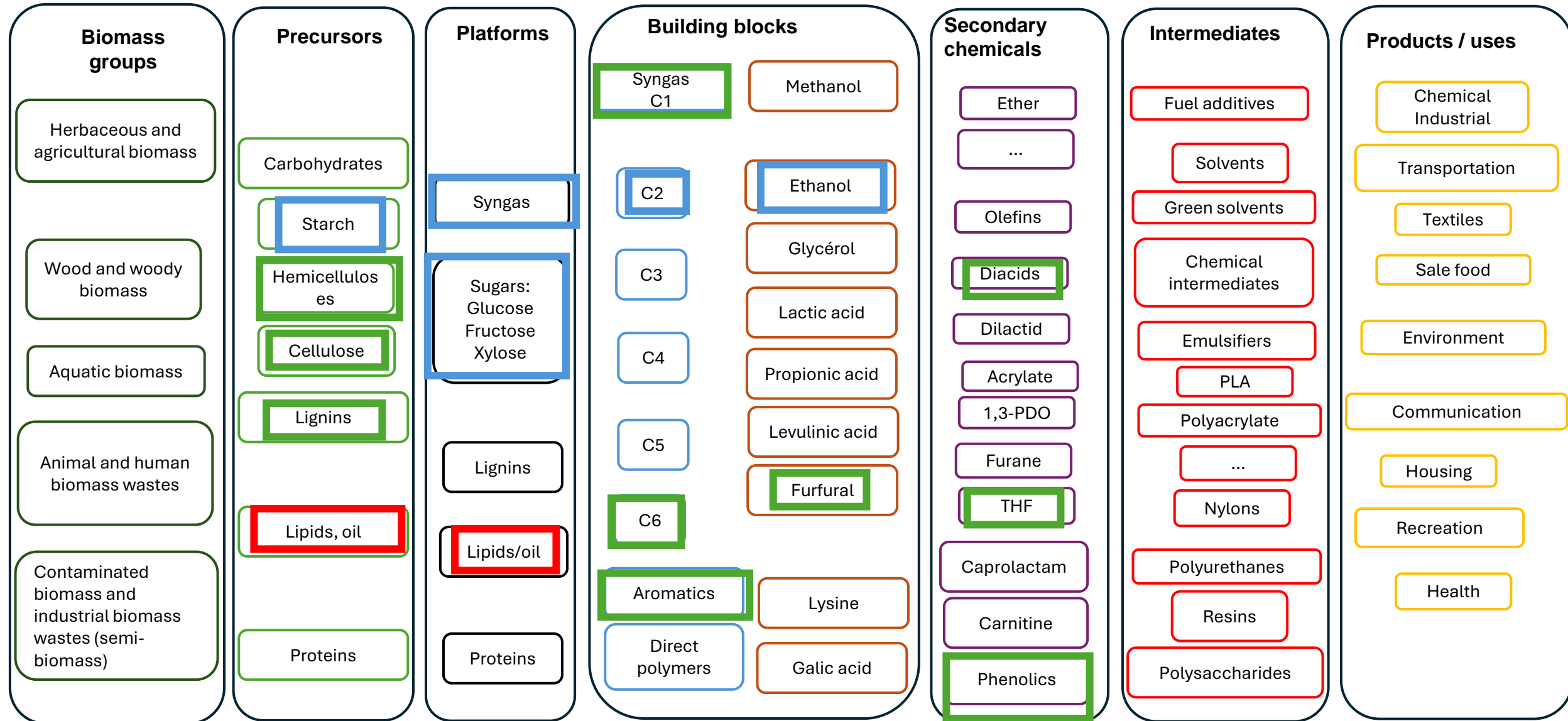
Les bioraffineries industrielles ont été identifiées comme la voie **la plus prometteuse** pour la création d'une **nouvelle industrie bio-basée nationale**.

# Classifications des bioraffineries

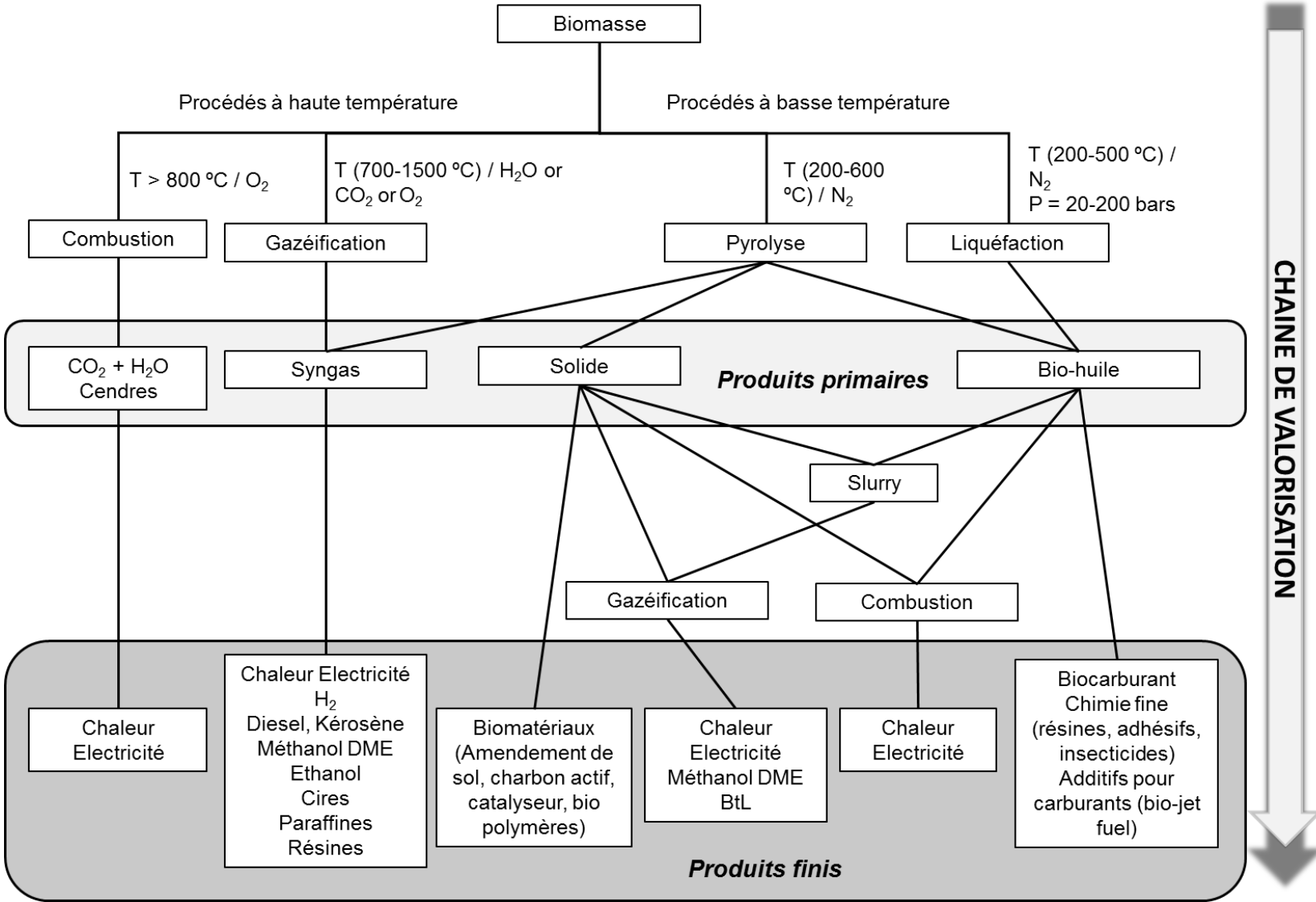
Phase I : Single feedstock / Primary products

Phase II : Single feedstock / Several products

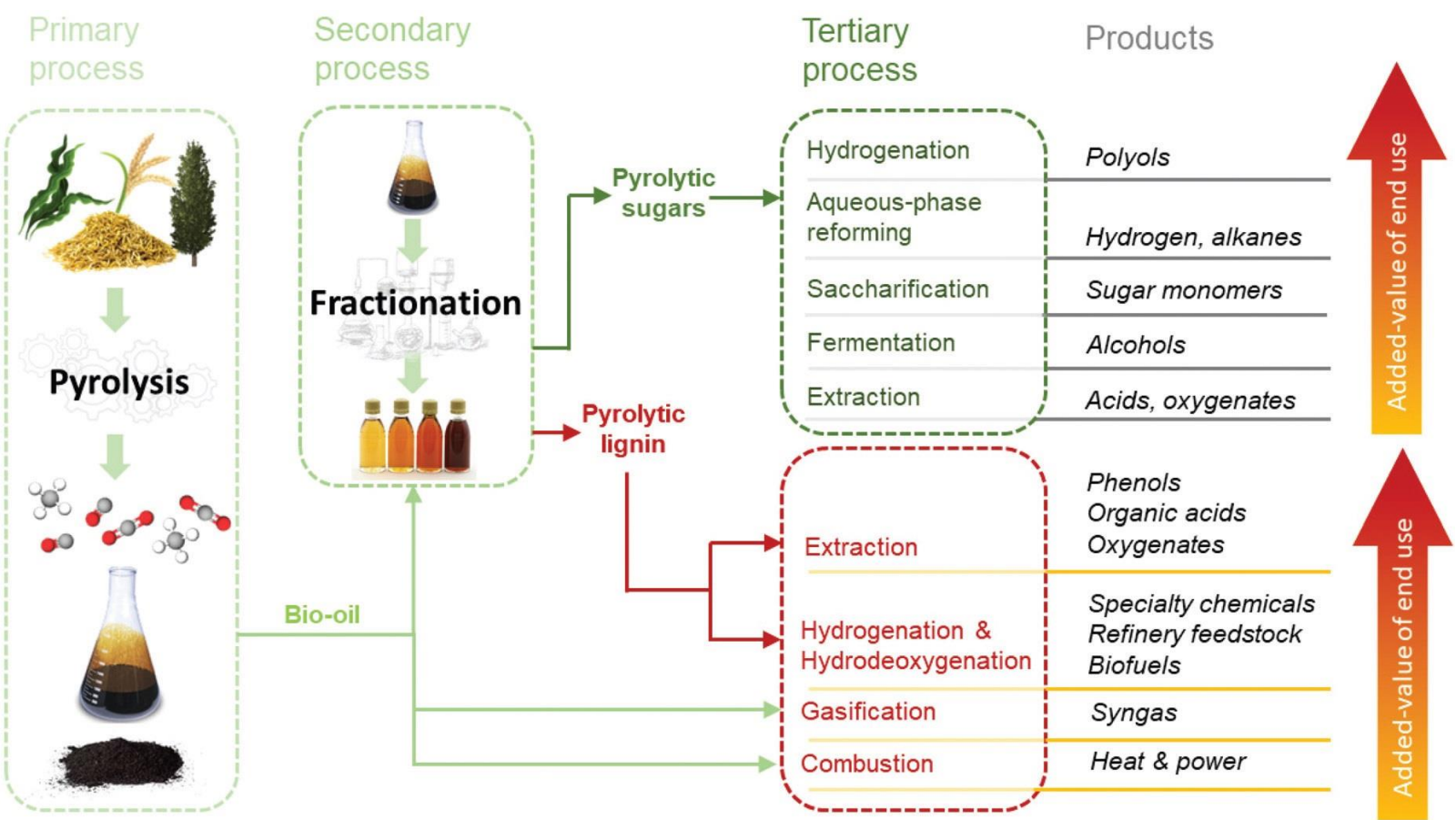
Phase III : Multiple feedstocks / Multiples products



# Plateformes thermochimiques



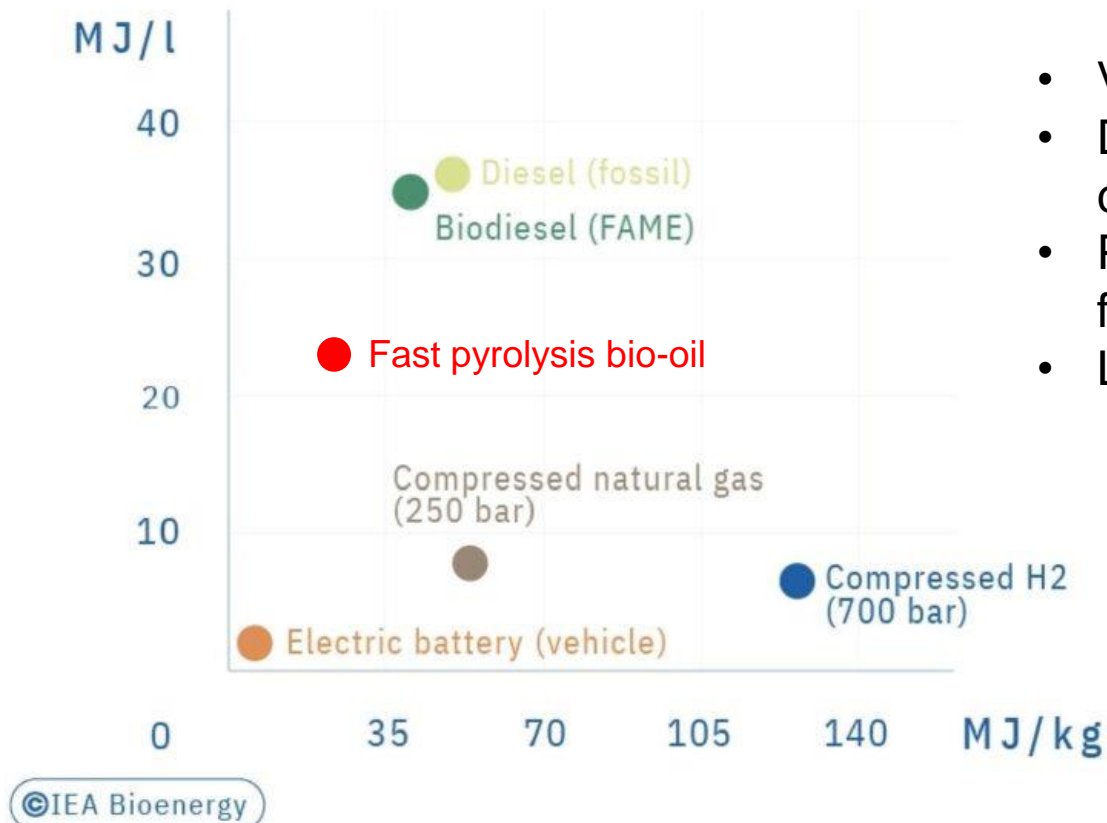
# Bioraffinerie pyrolytique autonome



[3] M. B. Figueirêdo, Green Chem., 2022, 24, 4680.

# Pourquoi produit-on des biocarburants liquides?

## ENERGY DENSITY OF FUELS



- Vecteur énergétique de transition
- Densité énergétique volumétrique et gravimétrique comparable à celle des énergies fossiles liquides actuels
- Puissances par rapport au volume embarqué pouvant faire avancer des véhicules lourds.
- Liquide stockable à bord

ASTM D 7544 [5]

ASTM D6866 [6]



[4] Graph from <https://www.ieabioenergyreview.org/reaping-the-multiple-benefits-of-bioenergy/> [5] <https://www.astm.org/d7544-12r17.html> [6]

<https://www.betalabservices.com/francais/biosources/astm-d6866.html>



# Pourquoi produit-on des biochars?

50°C - Ø = 7.9%

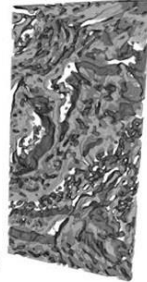


250 µm

350°C - Ø = 27.1%



450°C - Ø = 40.3%

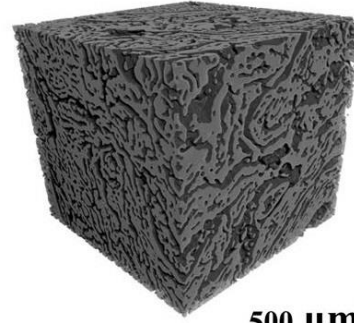


WSP

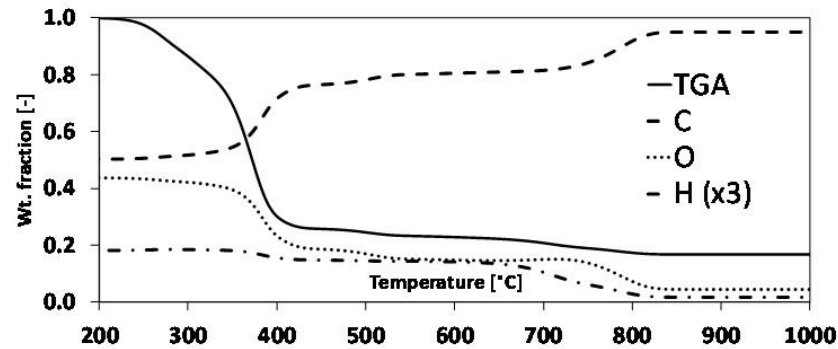
800°C - Ø = 29.4%



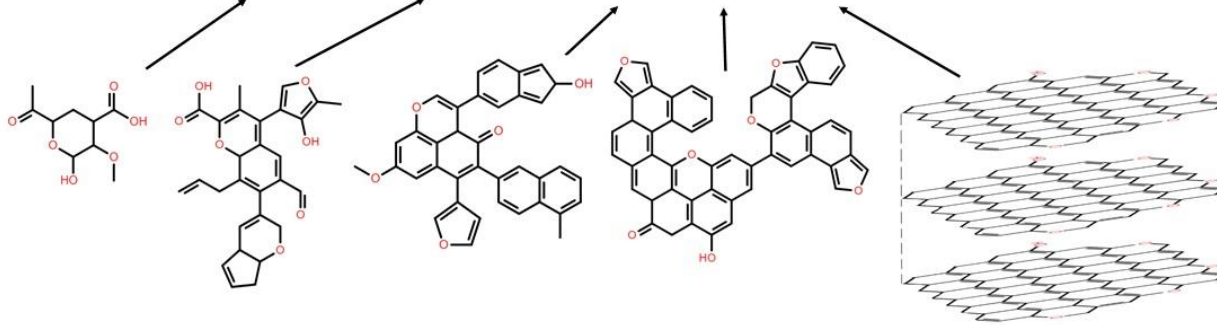
450°C



500 µm<sup>3</sup>

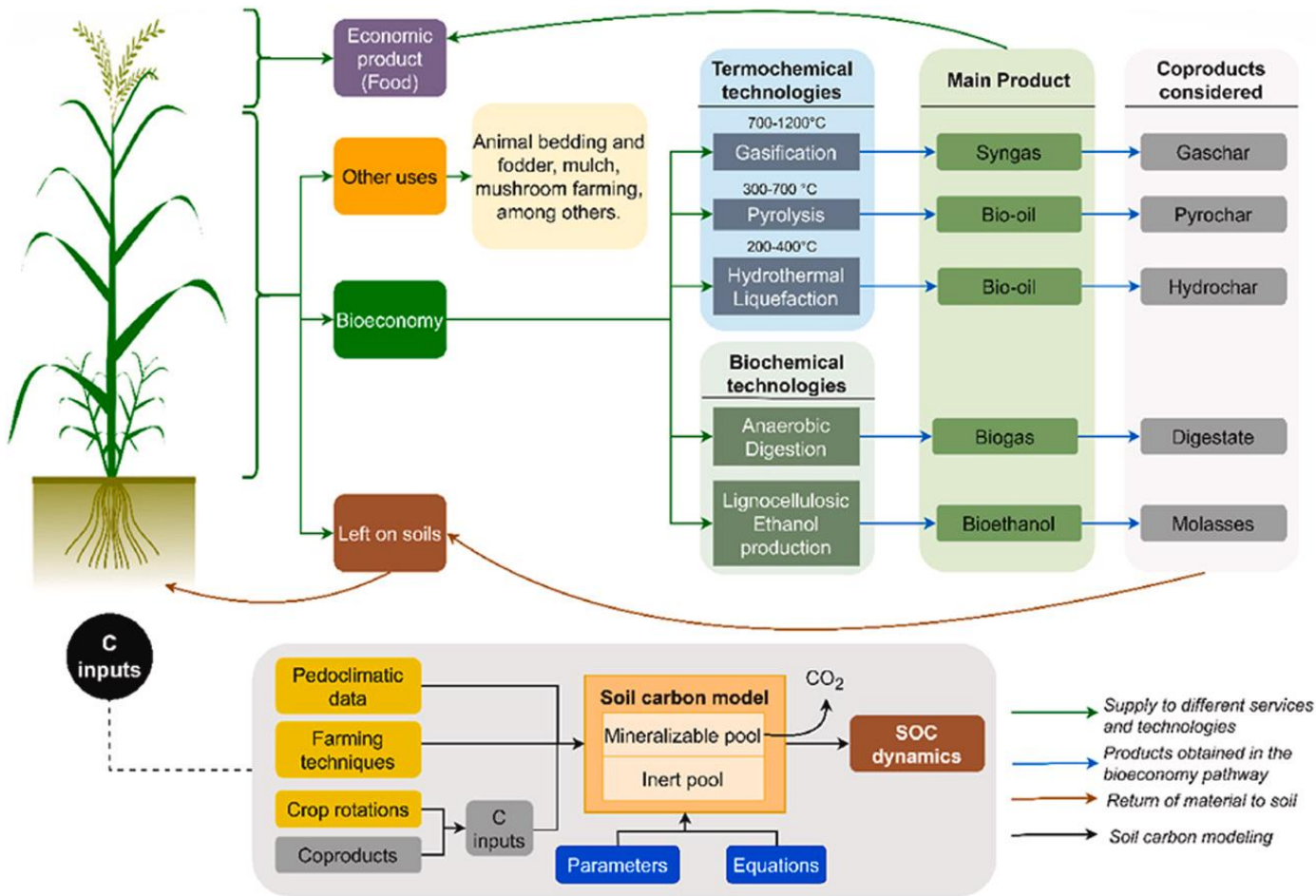


- Porosité hiérarchique
- Grande surface spécifique
- Chimie de surface
- Mouillabilité accrue
- Basicité de la surface



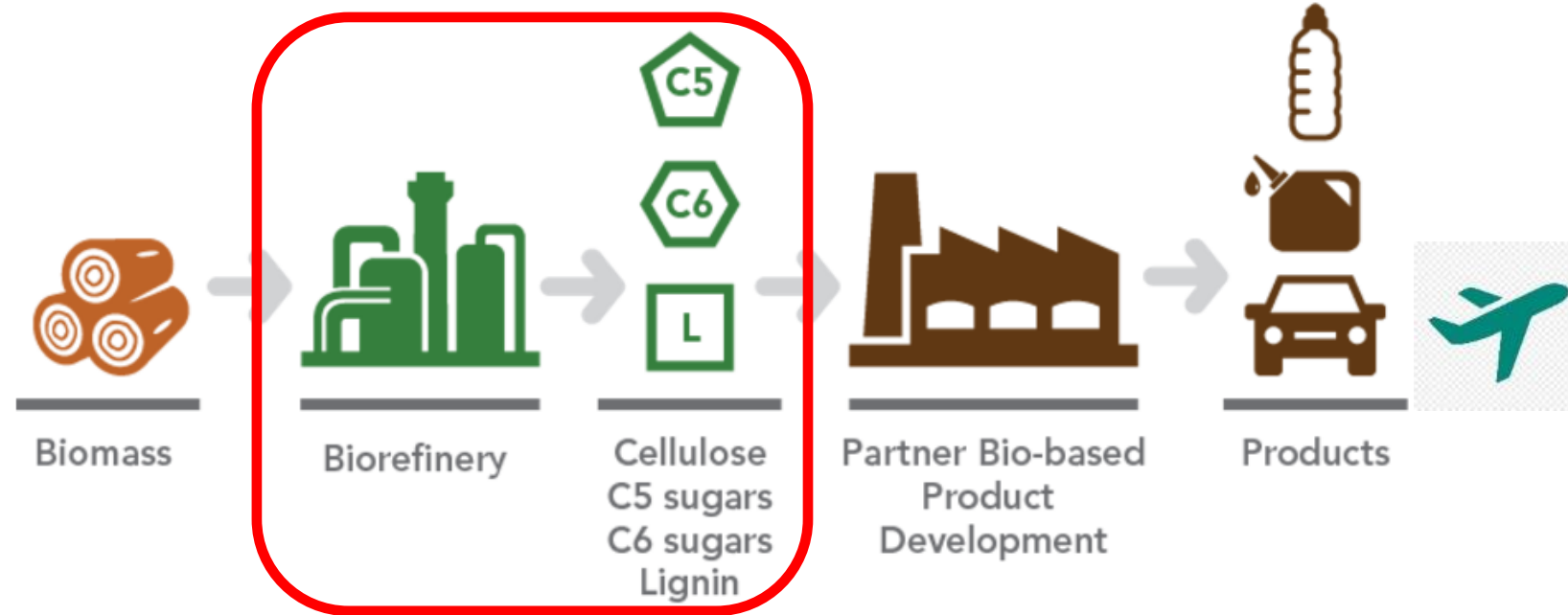


# Durabilité de bioraffinerie



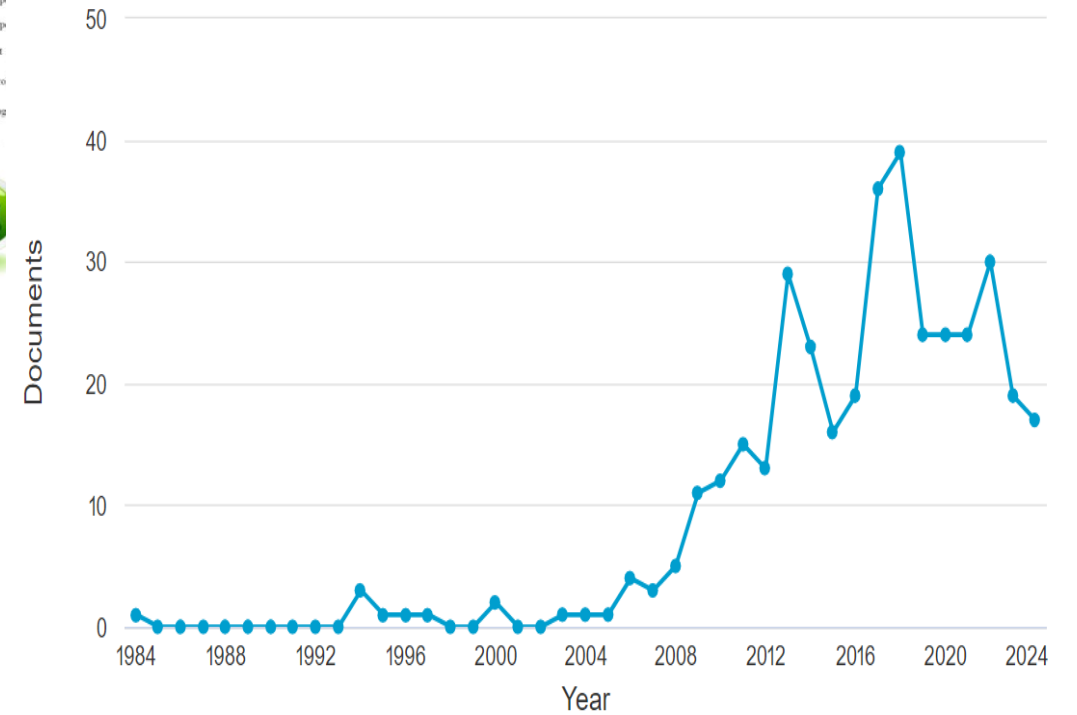
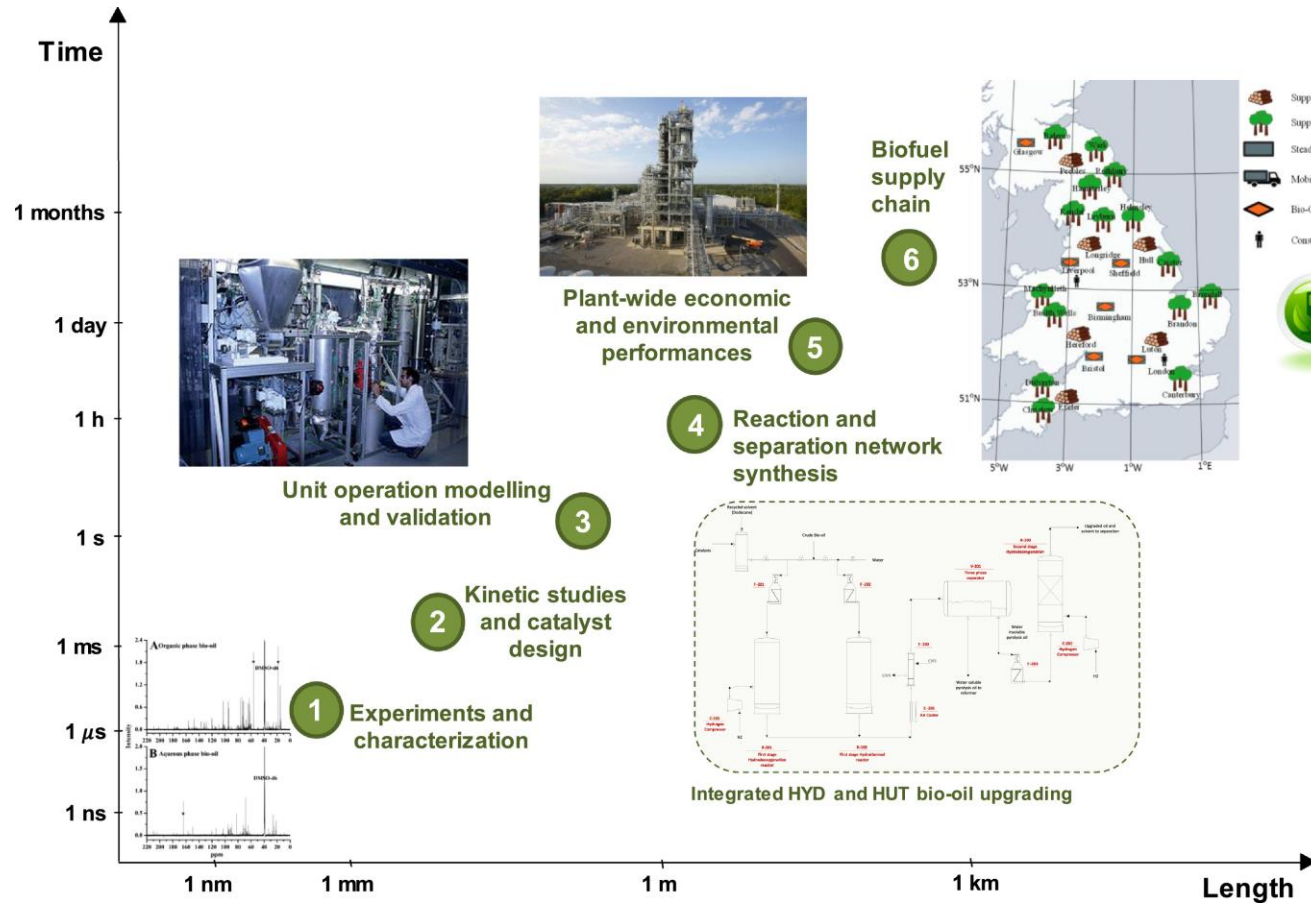
- Méthode d'analyse du cycle de vie
- Définition de la matière première
- Utilisation directe des terres a des conséquences environnementales.
- Prise en compte du modèle de carbone organique du sol (COS) indispensable.

# Concept de bioraffinerie emprunté / Enjeux

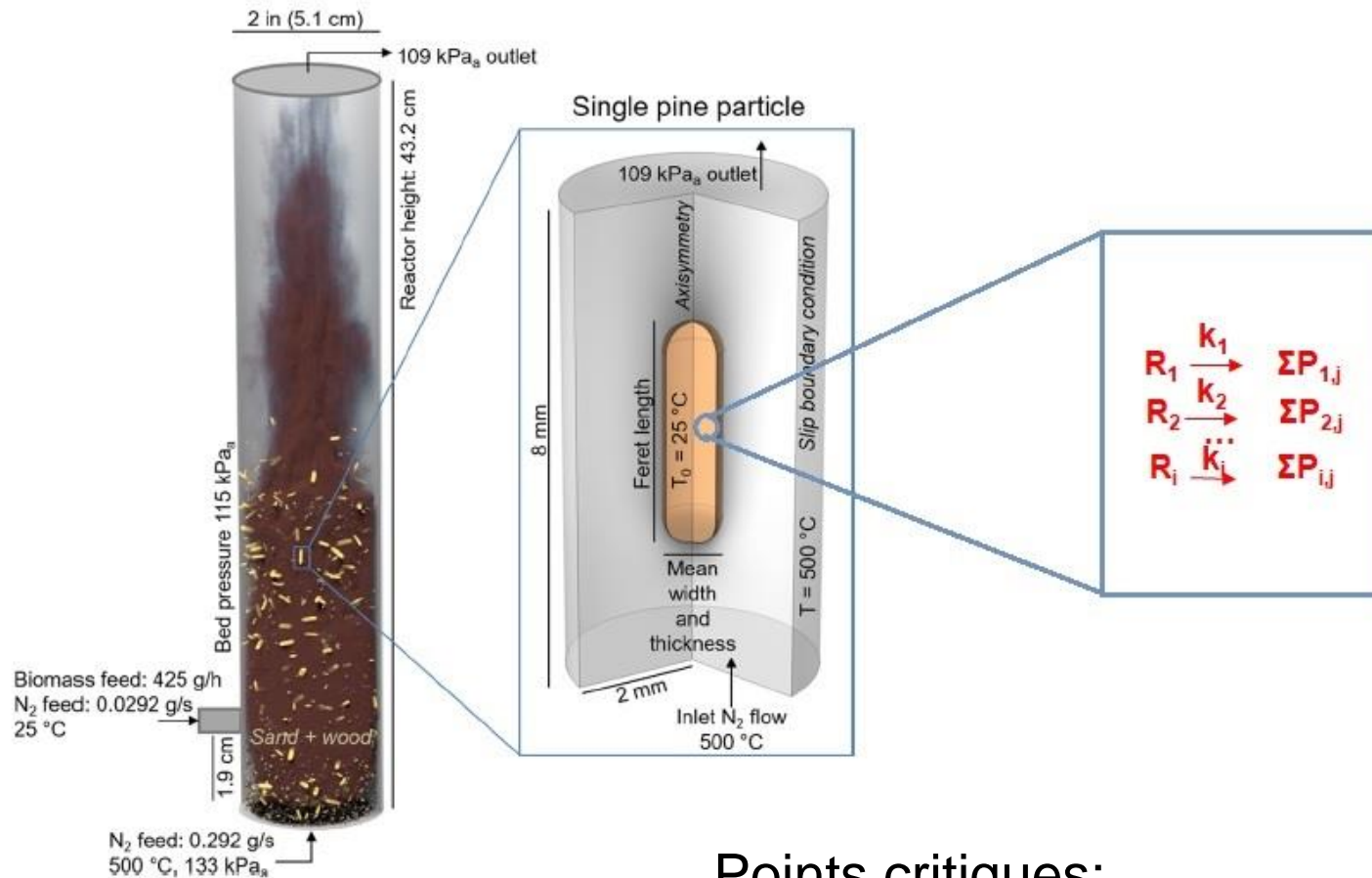


- Production de quantité intéressante et pureté suffisante;
- Séparation des molécules;
- Intensification des recherches nécessaires sur le couplage chimie-procédés et procédés;
- Mise à l'échelle des procédés les plus viables;
- Promotion de projets écoresponsables avec des matières premières sourcées durablement.

# Modélisation de la pyrolyse rapide



# Biomass fast pyrolysis - the most mature reactor models

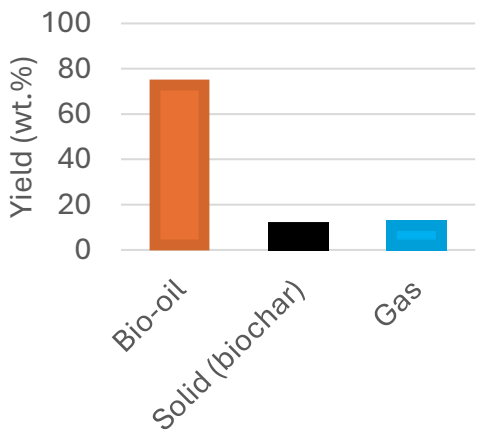


## Points critiques:

- Chauffage des particules et historique temps-température;
- Temps de séjour des particules et matières volatiles;
- Influence des phases de contact, de mélange et écoulements.

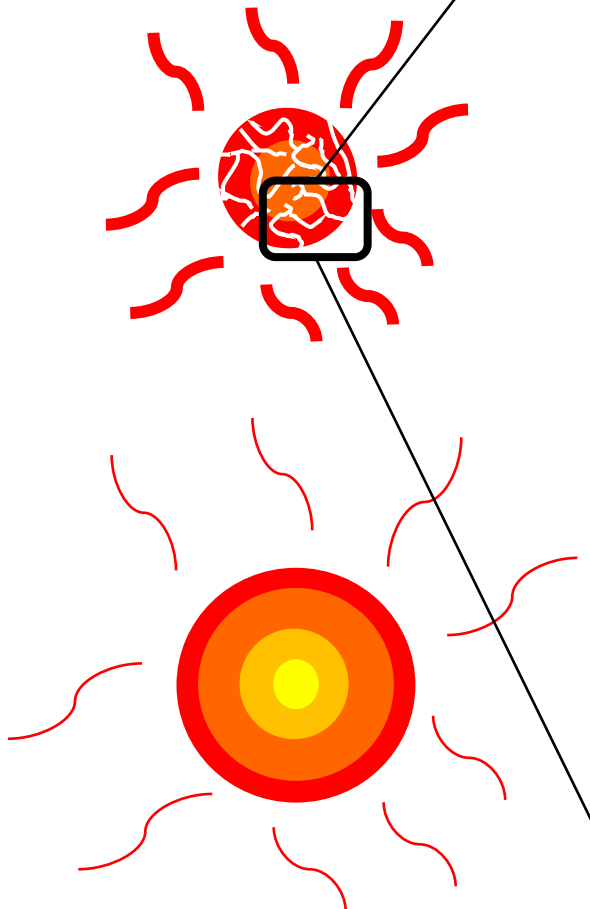
# Biomass fast pyrolysis

**Fast pyrolysis products and operating conditions [1]:**

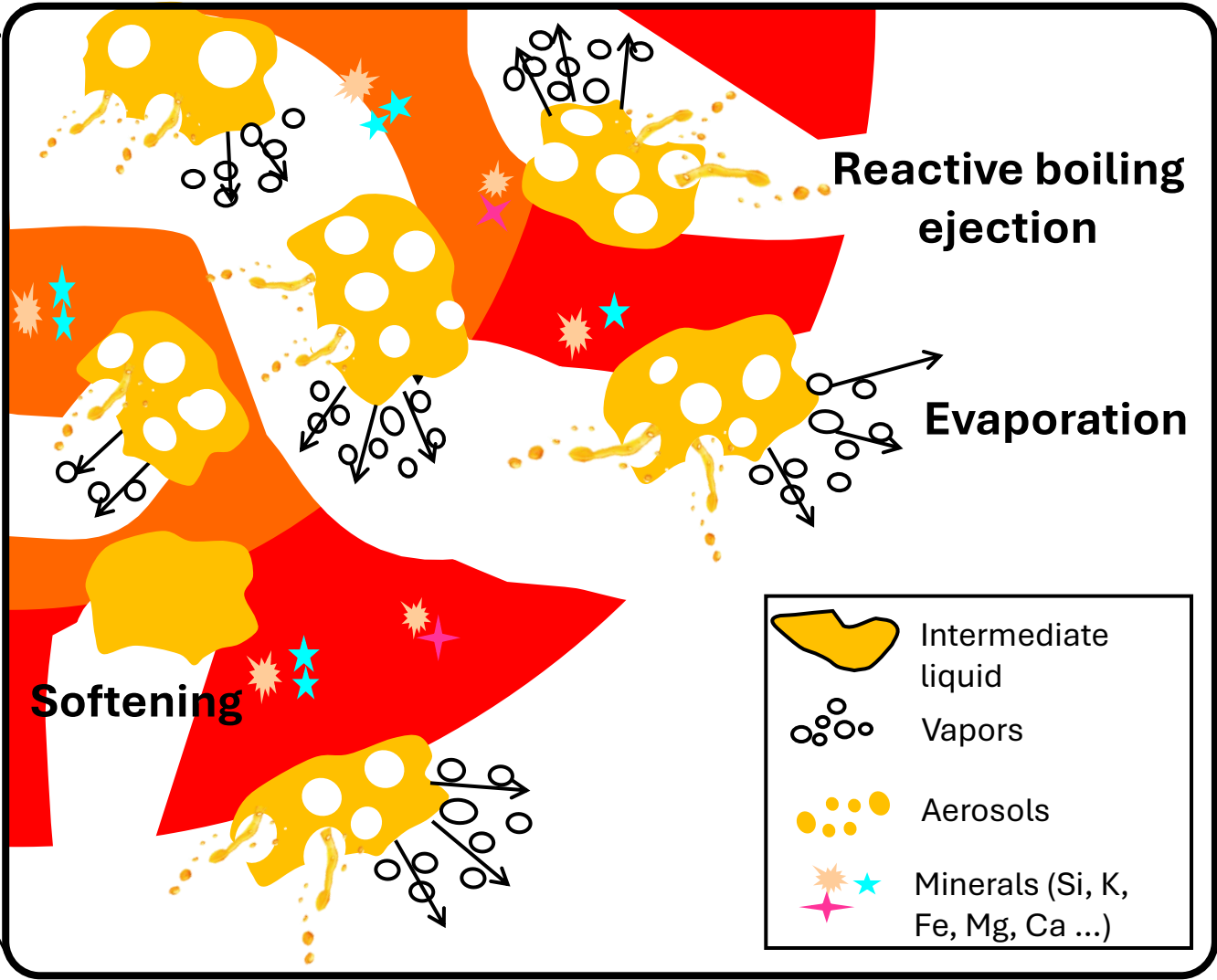


Temperature ~ 500 °C  
 Heating rate  $\beta$  ~ 500 °C/s  
 Volatile holding time < 2 s  
 Particle size < 1 mm

**Heat transfer:**  
 ■ Convection  
 ■ Radiation  
 ■ Conduction

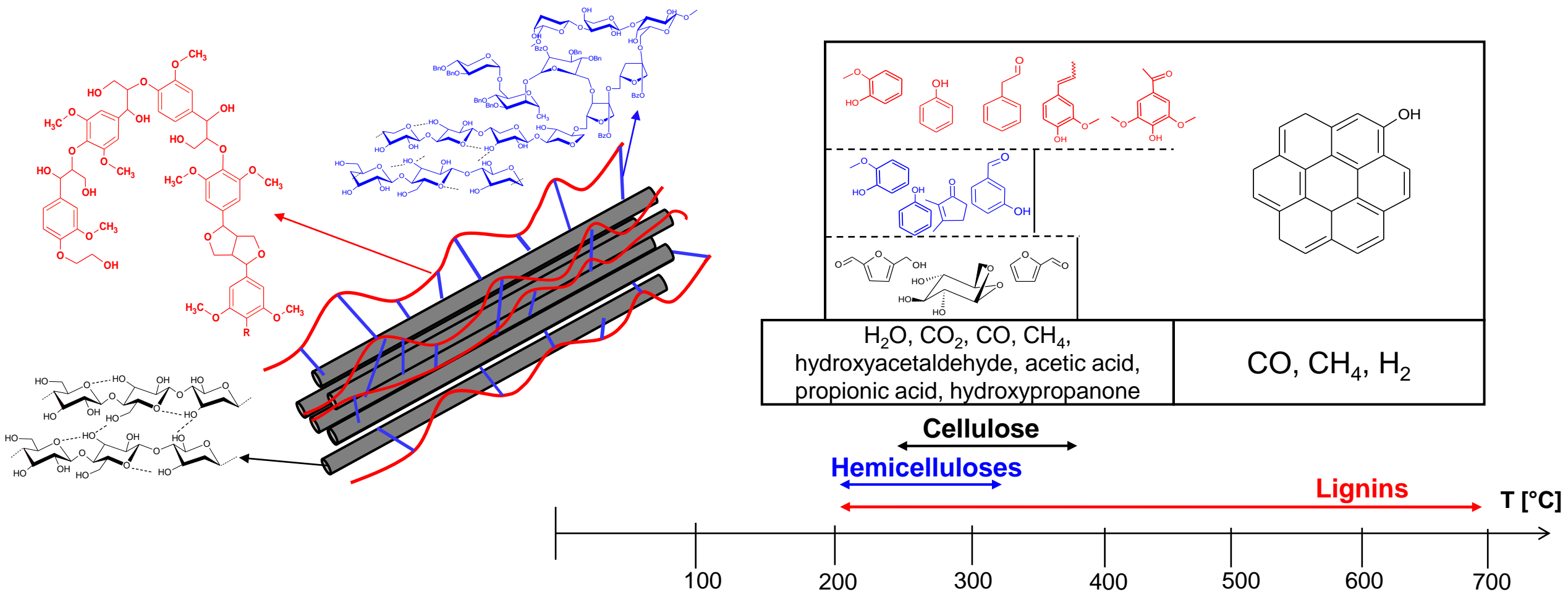


**Particle scale devolatilization**



[15] Bridgwater A.V. Biomass and Bioenergy 38 (2012) 68-94; [16] Nasfi et al., PhD Thesis defended in 2023.

# Lignocellulosic biomass



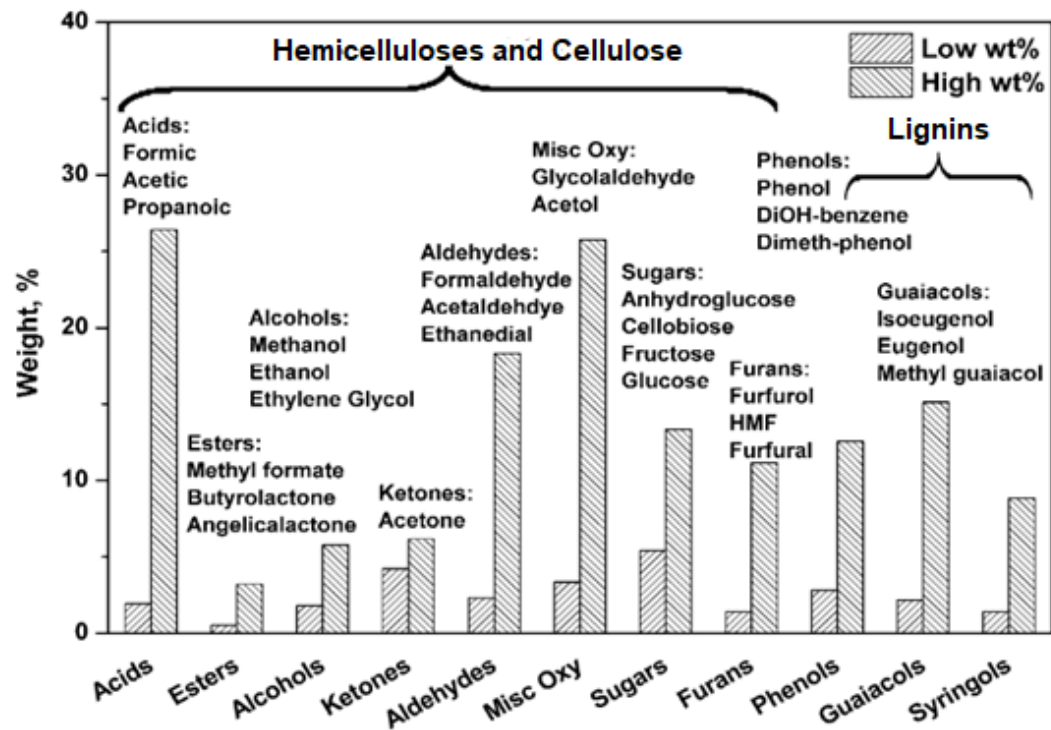
+ Extractives  
 + Inorganics (Si, K, Fe, Mg, Ca ...)

[17] Carrier *et al.*, Biomass and Bioenergy 35 (2011) 298-307.

[18] Collard *et al.*, Chapter 4: Fractionation of Lignocellulosic Material With Pyrolysis Processing (2016) 81-101.



# Fast pyrolysis bio-oil: Heterogeneous chemical composition



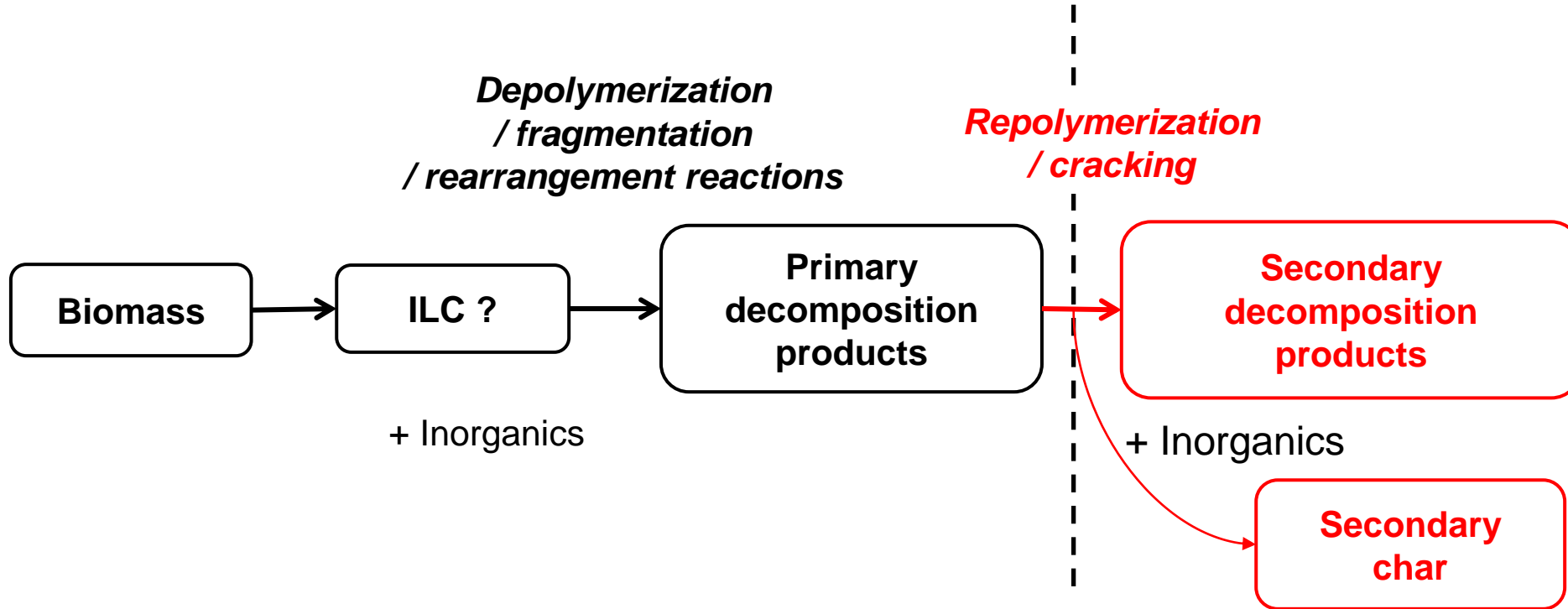
## Physico-chemical properties:

- pH < 2 ou 3<sup>[19]</sup>
- Chemically instable: oxygenated chemical compounds<sup>[20]</sup>
- High viscosity and density<sup>[20]</sup>
- Calorific value (dry basis) : 18-23 MJ/kg<sup>[21]</sup>
- Weak O/C (0.83-0.57)<sup>[4]</sup> & moderate H/C (1.13-1.35)<sup>[22]</sup>

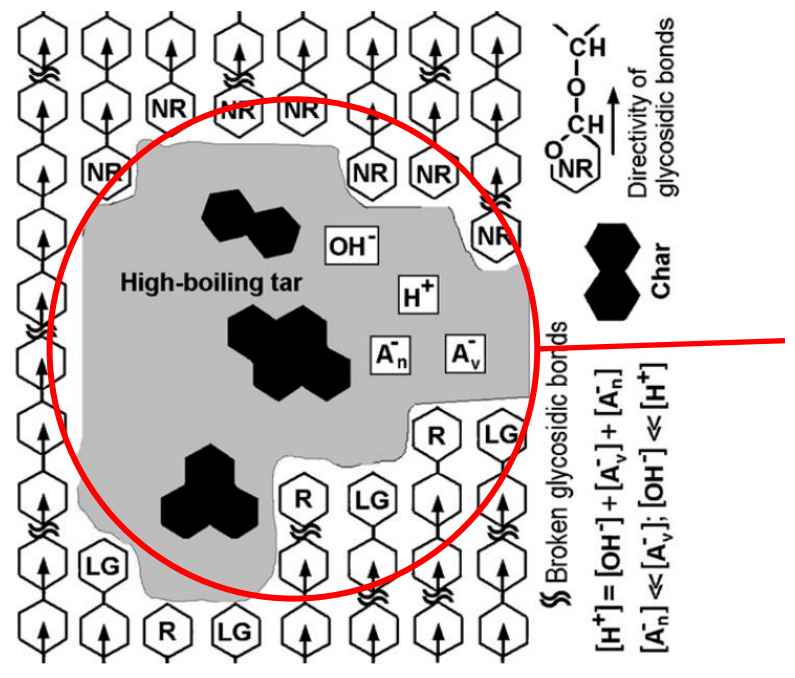
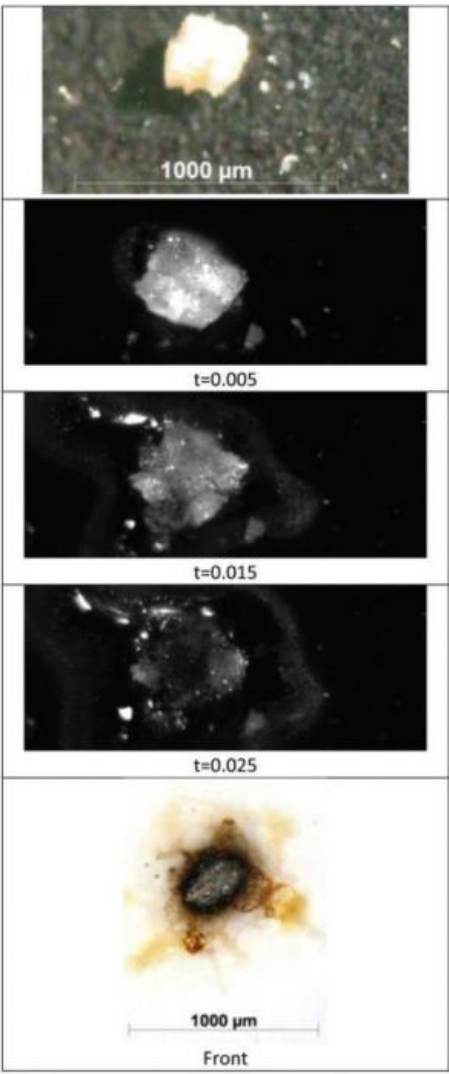
[19] Liu *et al.*, Chem. Soc. Rev 43 (2014) 7594; [2] Black *et al.*, RCS Adv 10 (2020) 10046; [20] Elmeri *et al.*, Energy Fuels 36 (2022) 3654.  
[21] Mettler *et al.*, Energy & Environmental Science 5 (2012) 5414; [22] Huang *et al.*, Energy Fuels 30 (2016) 9524.



# Primary and secondary reactions



# The liquid reaction environment



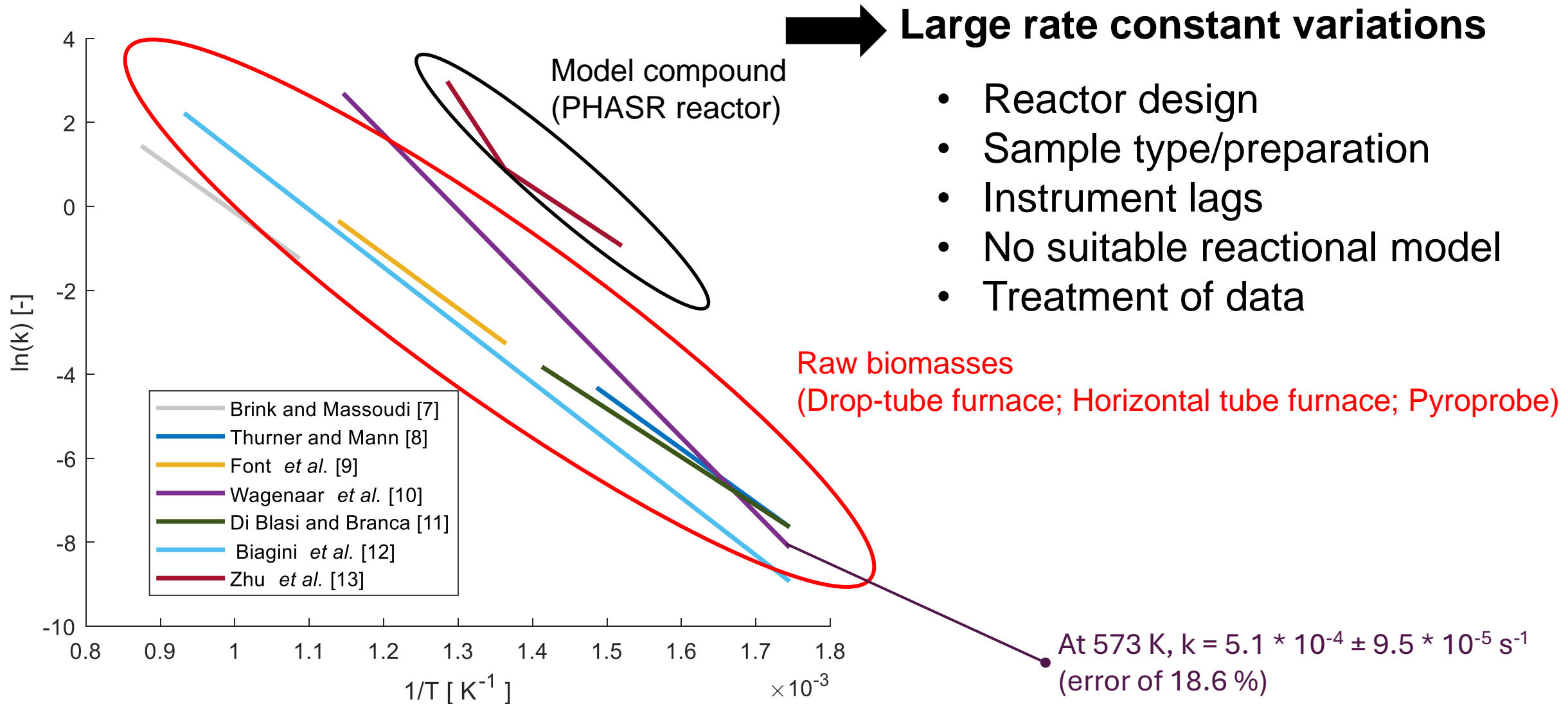
ILC lifetime:  
50-120 ms

Two-phase model[16]

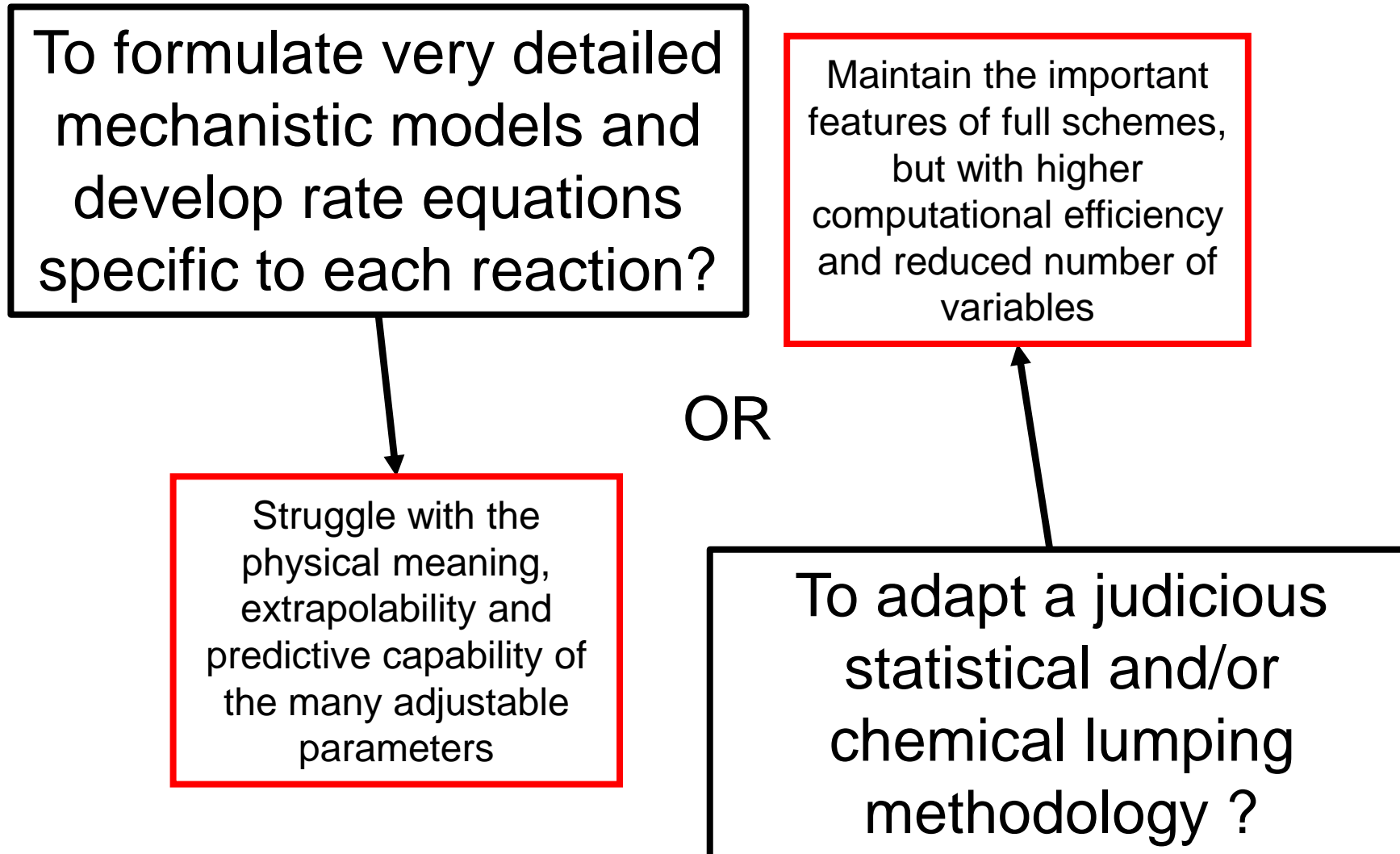
Evolution of ILC during fast pyrolysis.[15]

[23] Taken from Carlsson et al. (2013).; [24] Taken from Mamleev et al. (2009)

# Single-step model using high heating rates

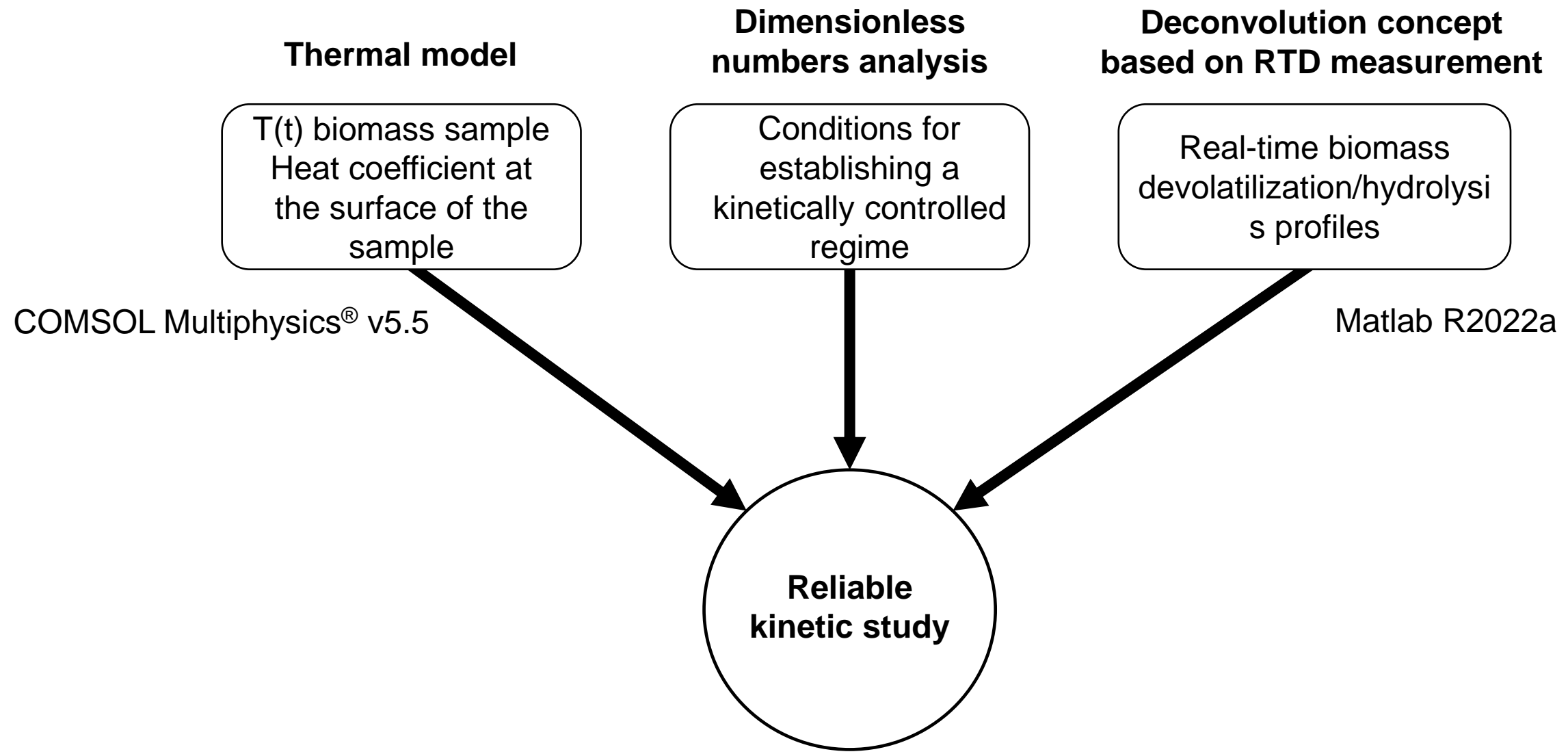


# *Kinetic modelling approach*



# Une méthodologie expérimentale commune

RTD: residence time distribution



# Mesurer, déterminer et modéliser les cinétiques globales

- **Analyse thermique (lumped)** – approche non stoechiométrique :  $A \xrightarrow{k} B$   
*avec A et B des espèces regroupées*

Suivi en fonction de la dégradation et/ou de la production et réactivité associée, cinétique apparente/globale

- **Analyse semi-détaillée (semi-lumped)** – approche stoechiométrique :  $\alpha A \xrightarrow{k_i} \beta B$   
*avec A et B des molécules/regroupements d'isomères  
et  $\alpha, \beta$  coefficients stoechiométriques*

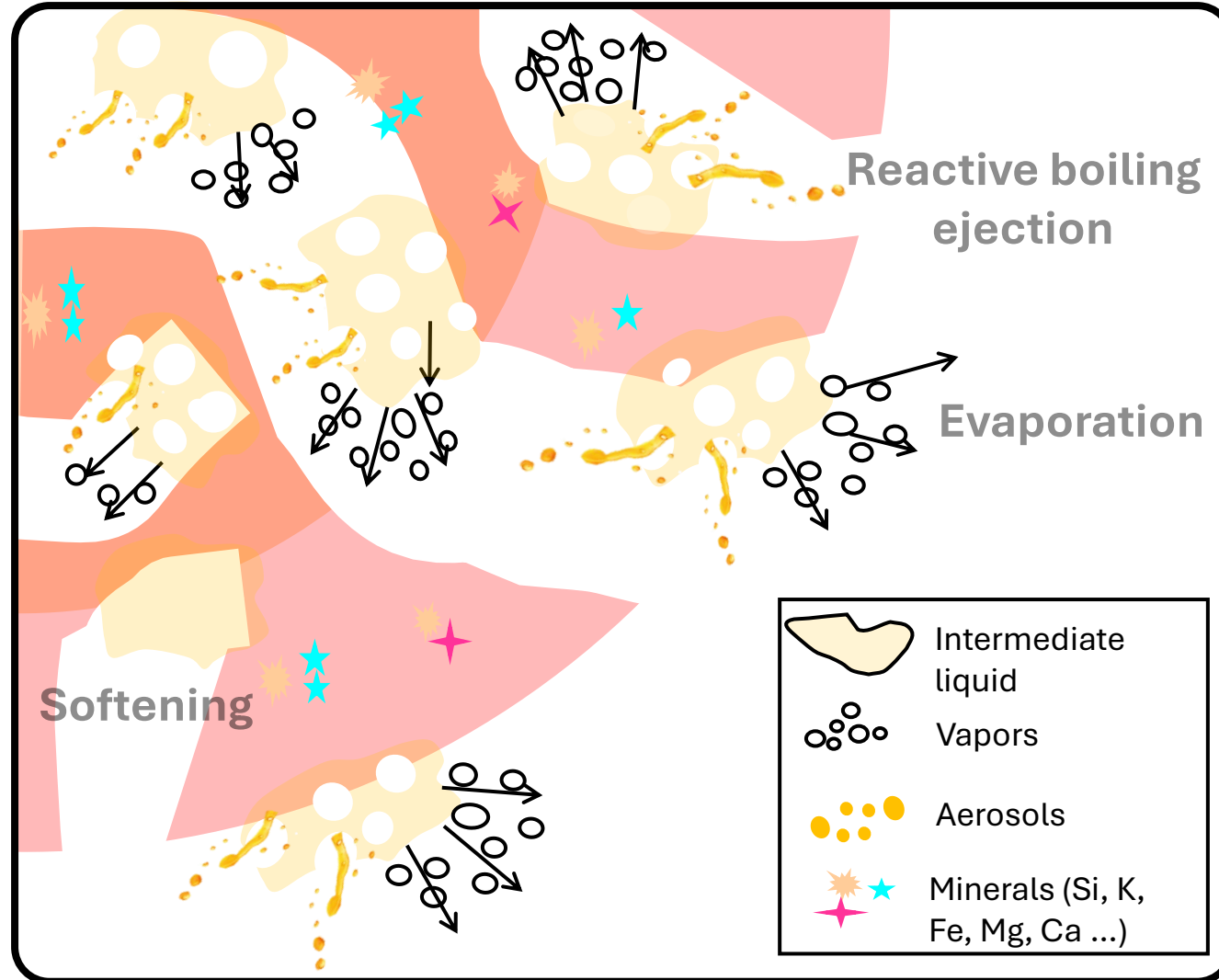
Suivi en fonction de la dégradation et/ou de la production, rendements et cinétiques apparentes/globales

- **Analyse détaillée** – approche mécanistique :  $A \xrightarrow{k} B$   
*avec A et B des molécules*

Mécanismes, voies de dégradation, cinétiques intrinsèques

# Etude de la dévolatilisation du solide

## Thin-film devolatilization

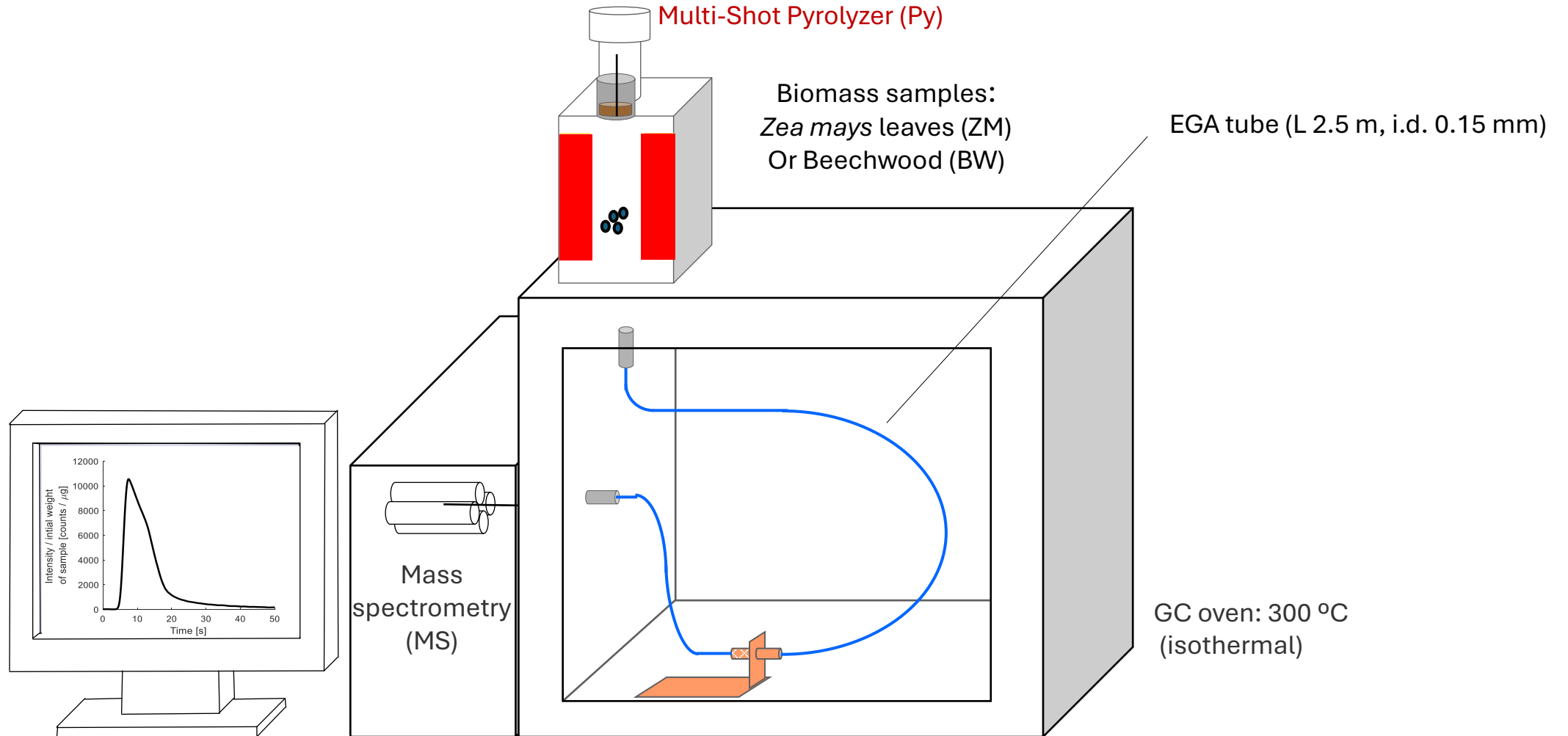




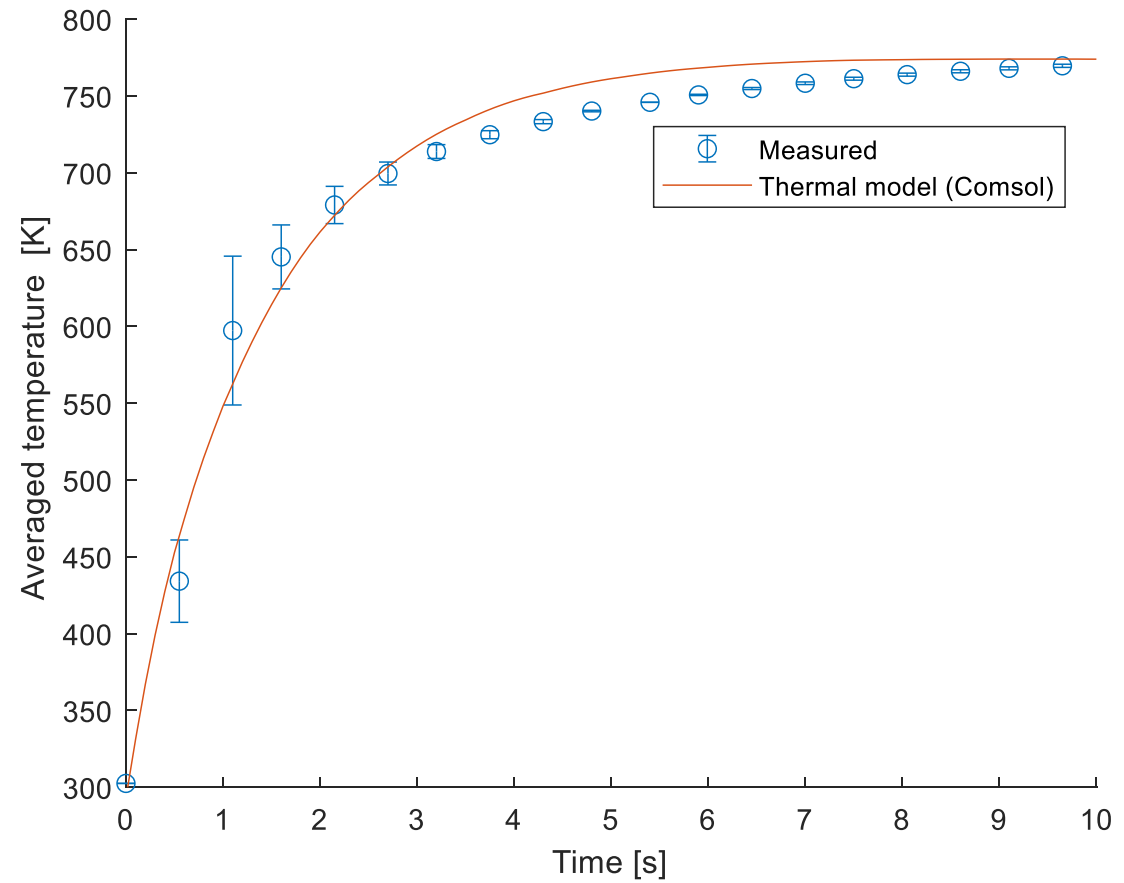
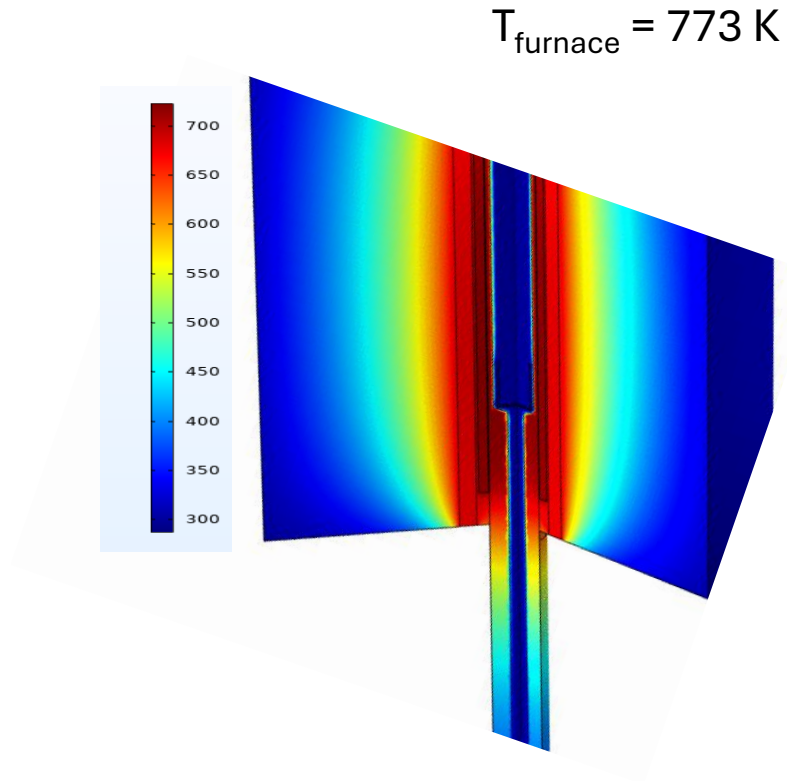
# Appareillage pour le système réactif solide

EGA: Evolved gas analysis  
L: EGA tube length (m)  
i.d.: Inside diameter (mm)

Film mince de biomasse et non réactif [32]:



# Modélisation thermique



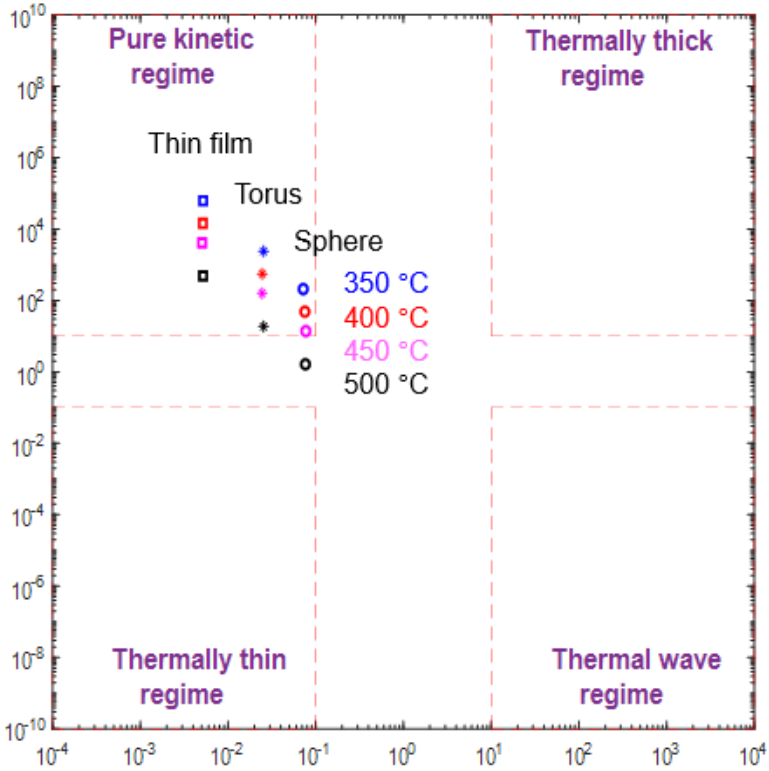
**Model validation**

# Pyrolysis regime mapping

$$U = 165 - 208 \text{ W/m}^2 \text{ K}$$

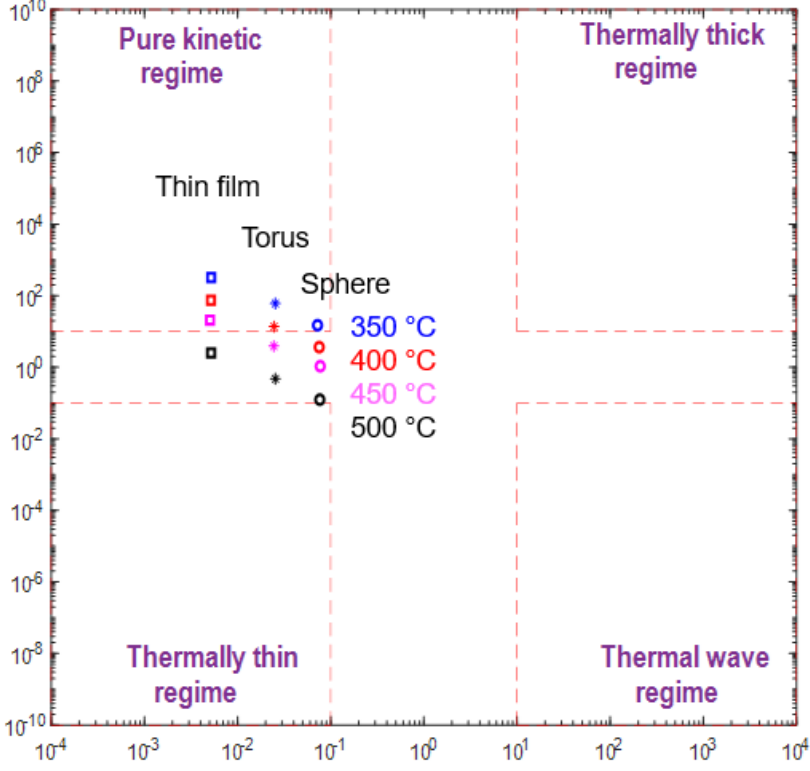
$U$ : Overall external heat transfer coefficient ( $\text{W/m}^2\text{K}$ )     $k$ : rate constant ( $\text{s}^{-1}$ )  
 $\lambda$ : Thermal conductivity ( $\text{W/m K}$ )     $c_p$ : Heat capacity ( $\text{J/kg K}$ )  
 $L_c$ : Characteristic length( m)     $\rho$ : density ( $\text{kg/m}^3$ )

$$Py = \frac{\tau_{\text{reaction}}}{\tau_{\text{conduction}}} = \frac{\lambda}{C_p L^2 k \rho}$$



$$Bi_{,T} = \frac{\tau_{\text{conduction}}}{\tau_{\text{external heat}}} = \frac{U L}{\lambda}$$

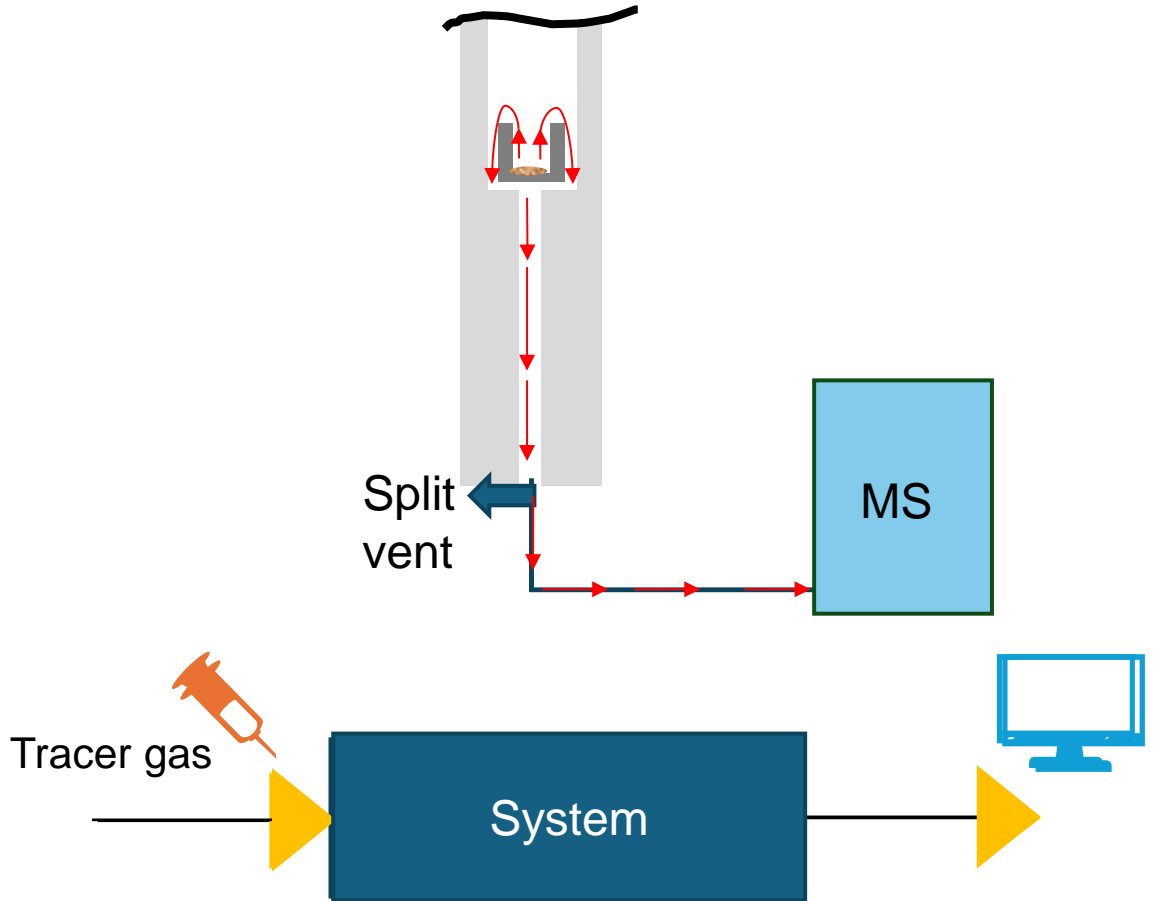
$$Py' = \frac{U}{\tau_{\text{external heat}}} = \frac{U}{C_p L k \rho}$$



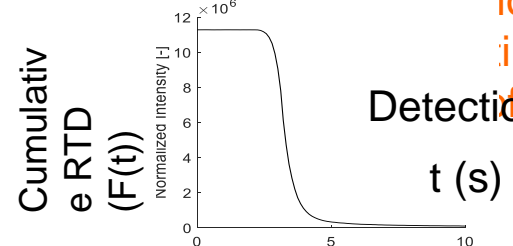
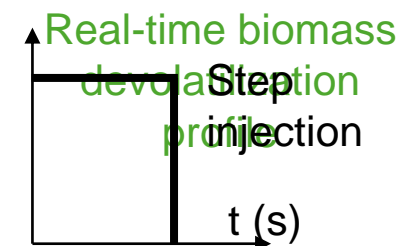
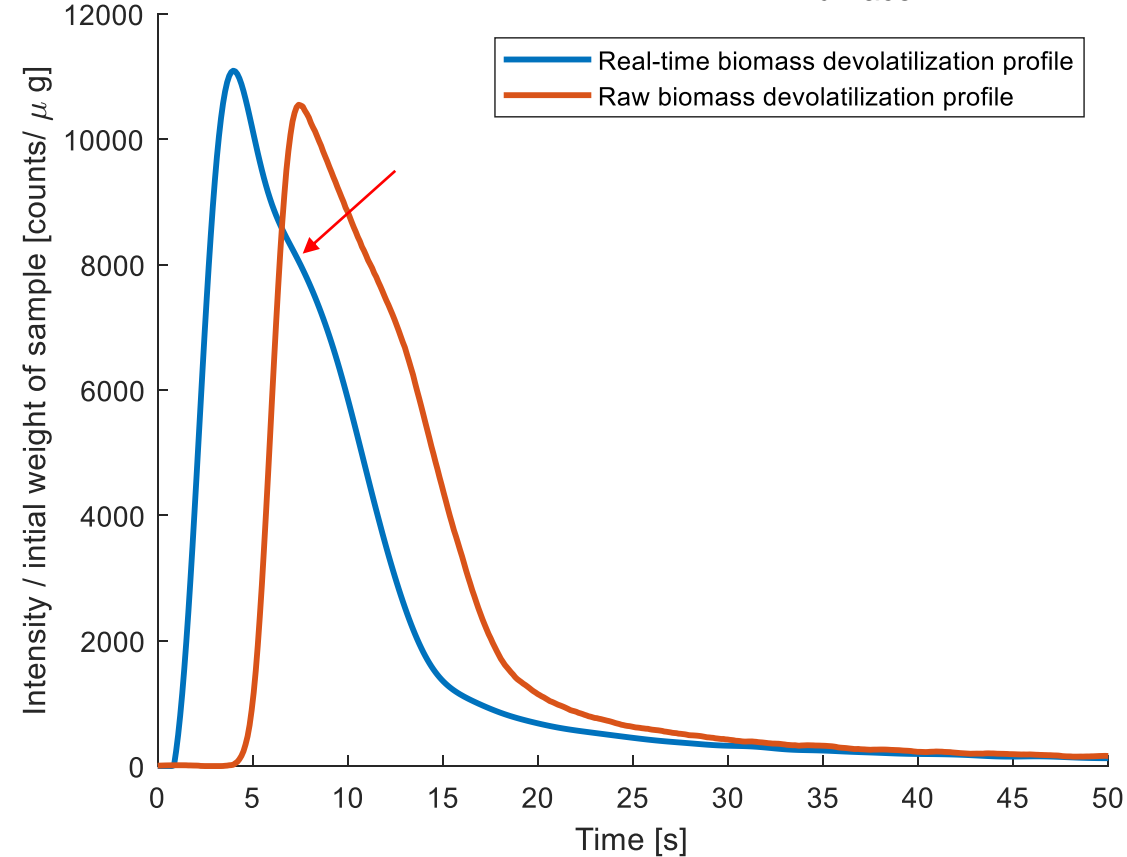
**Negligible internal heat transfer,  $Bi_{,T} \ll 1$  &  $Py \gg 1$**

**Mass sample  $\leq 50 \mu\text{g}$  / Accurate arrangement: Thin-film  
 Temperature  $\leq 450 \text{ }^\circ\text{C}$ ,  $Bi_{,T} \ll 1$  &  $Py' \gg 1$**

# Deconvolution technique for kinetic information reconstruction



Beechwood, at  $T_{\text{furnace}} = 723 \text{ K}$



$$E(t) = \frac{dF(t)}{dt}$$

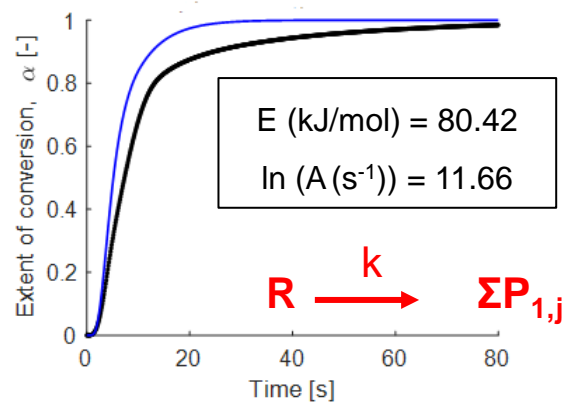
**Correction of the delay in the detection of pyrolysis products by the MS**

RTD: Residence time distribution

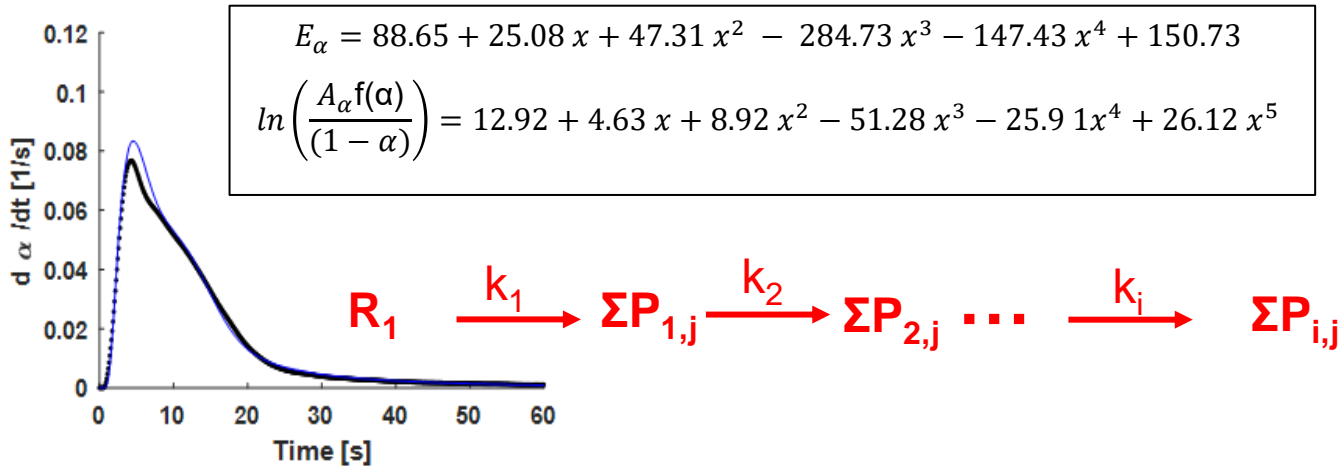
# Global kinetic modelling

• Experiment (BW, at  $T_{\text{furnace}} = 723 \text{ K}$ )  
 — Model

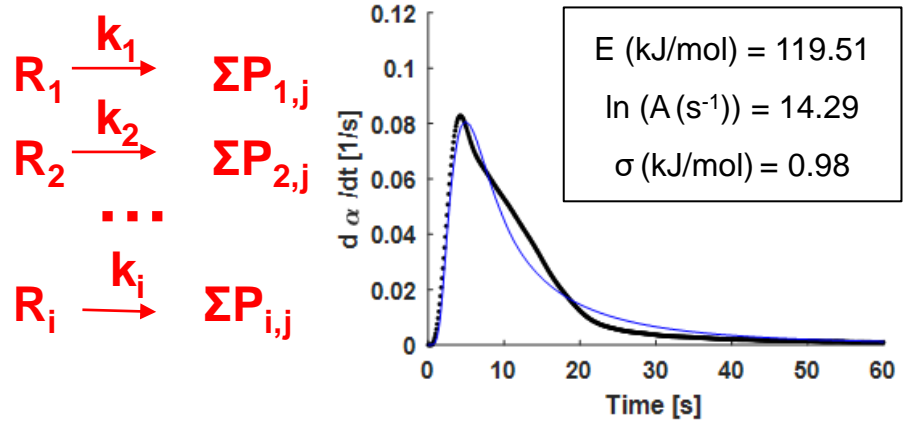
CAEM



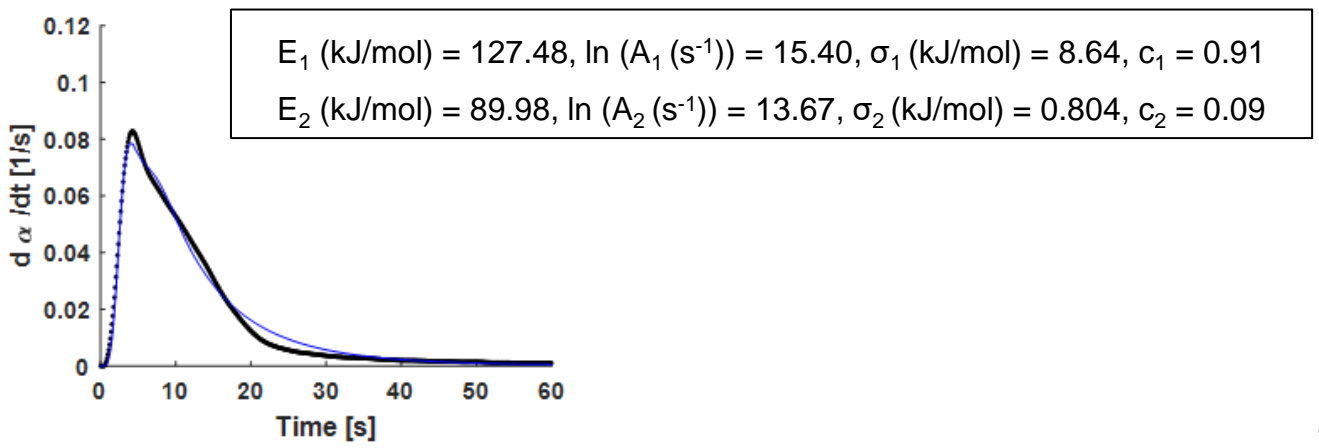
VAEM



1G-DAEM

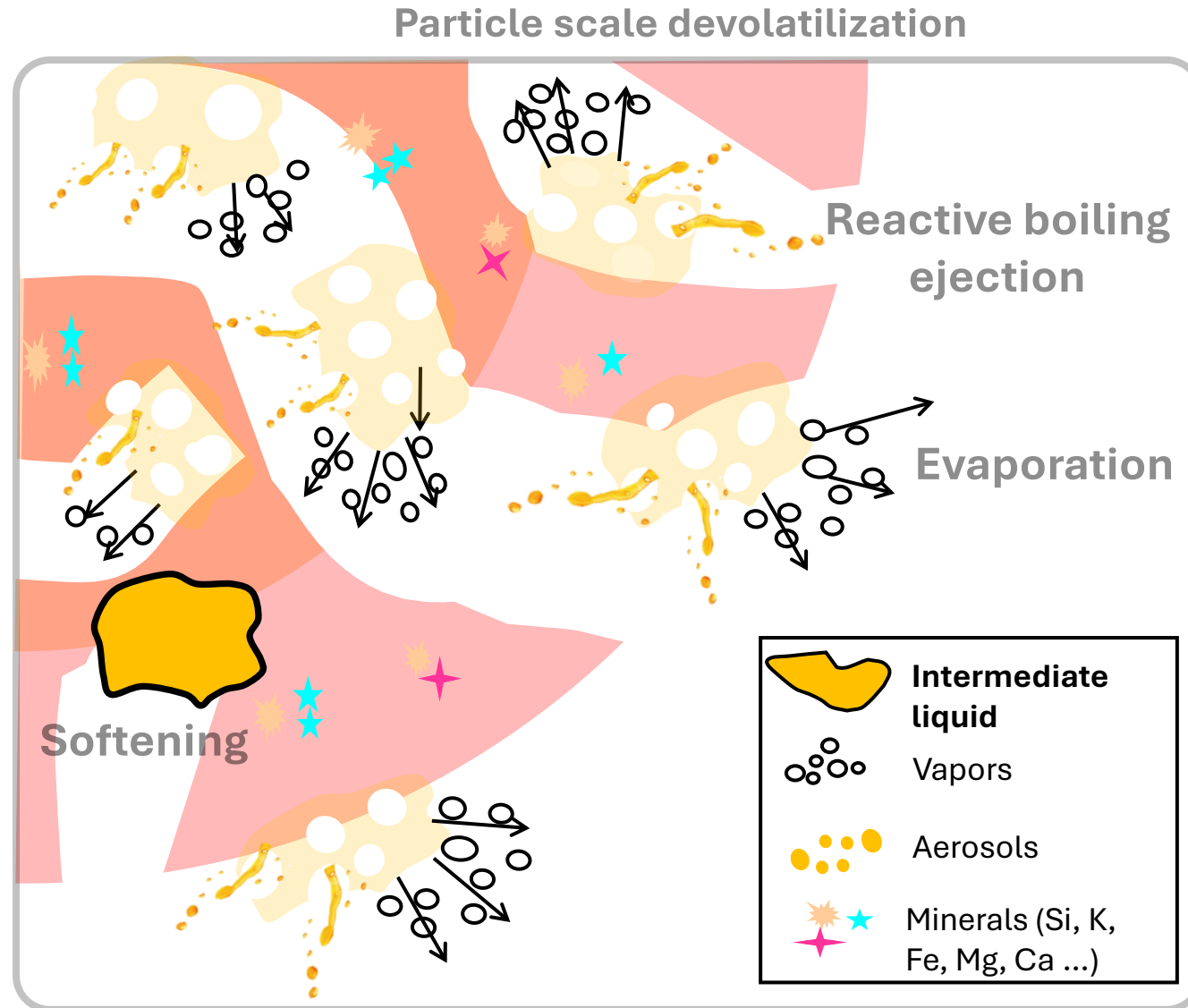


2G-DAEM

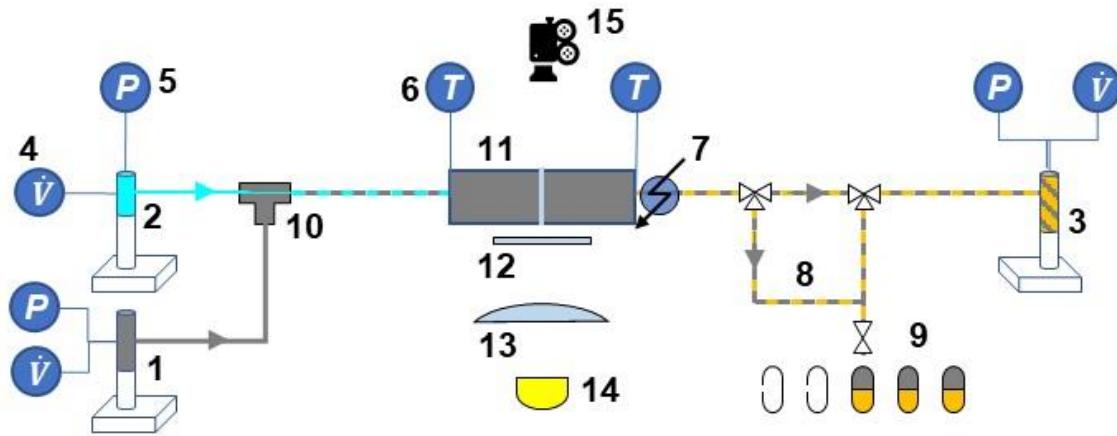


[33] Nasfi et al., Journal of Analytical and Applied Pyrolysis, 2023, 174, 106128

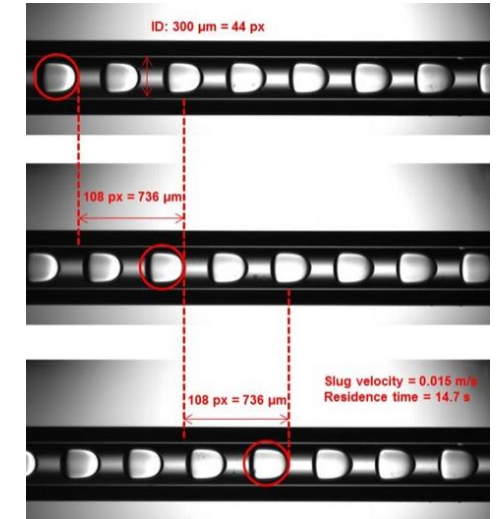
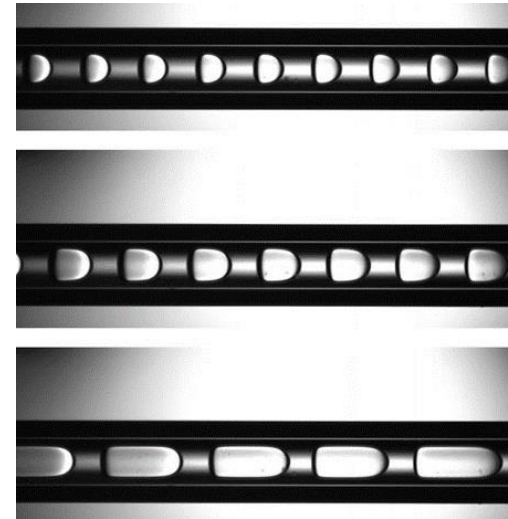
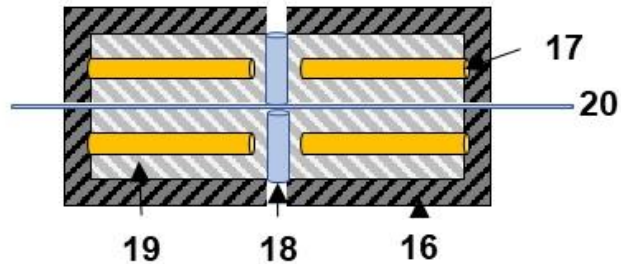
# Etude de la phase condensée réactive



# Appareillage pour le système réactif liquide



11 : sectional view of the heating device



1 syringe pump PDMS / 2 syringe pump aqueous solution / 3 syringe pump phases mixture / 4 volumetric flow rate controller / 5 pressure transducer / 6 temperature indicator (thermocouple) / 7 cooling device (air flow) / 8 sampling loop / 9 collecting samples / 10 coaxial injection device / 11 heating device / 12 frosted glass / 13 lens / 14 high power LED / 15 highspeed camera / 16 insulating coating (mica) / 17 heating cartridge / 18 quartz cylinder / 19 aluminium block / 20 micro-capillary.



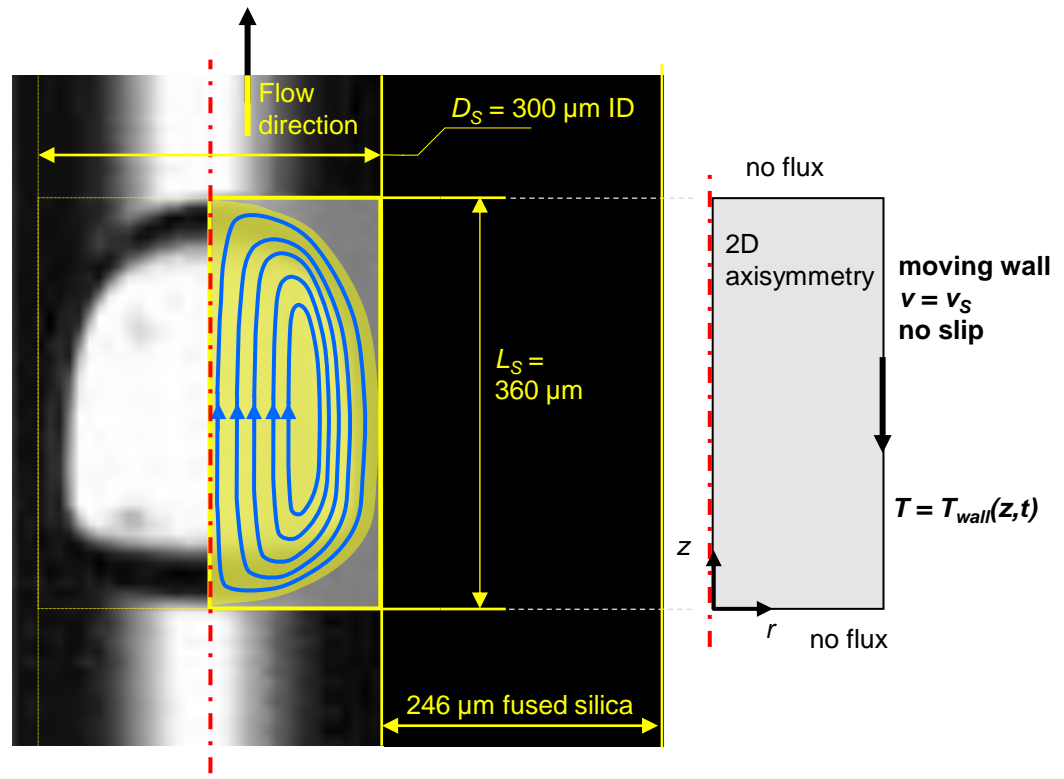
# Analyse dimensionnelle

$$Pe_M = \frac{L_S v_S}{D_{glucose}} = 35 - 540$$

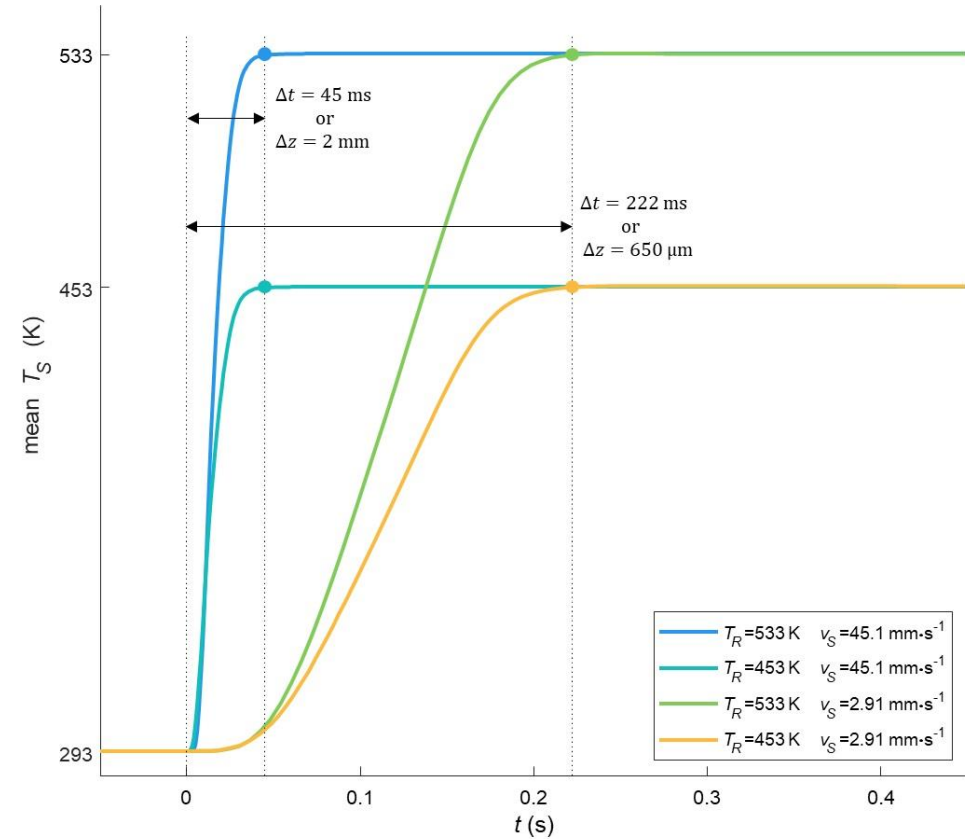
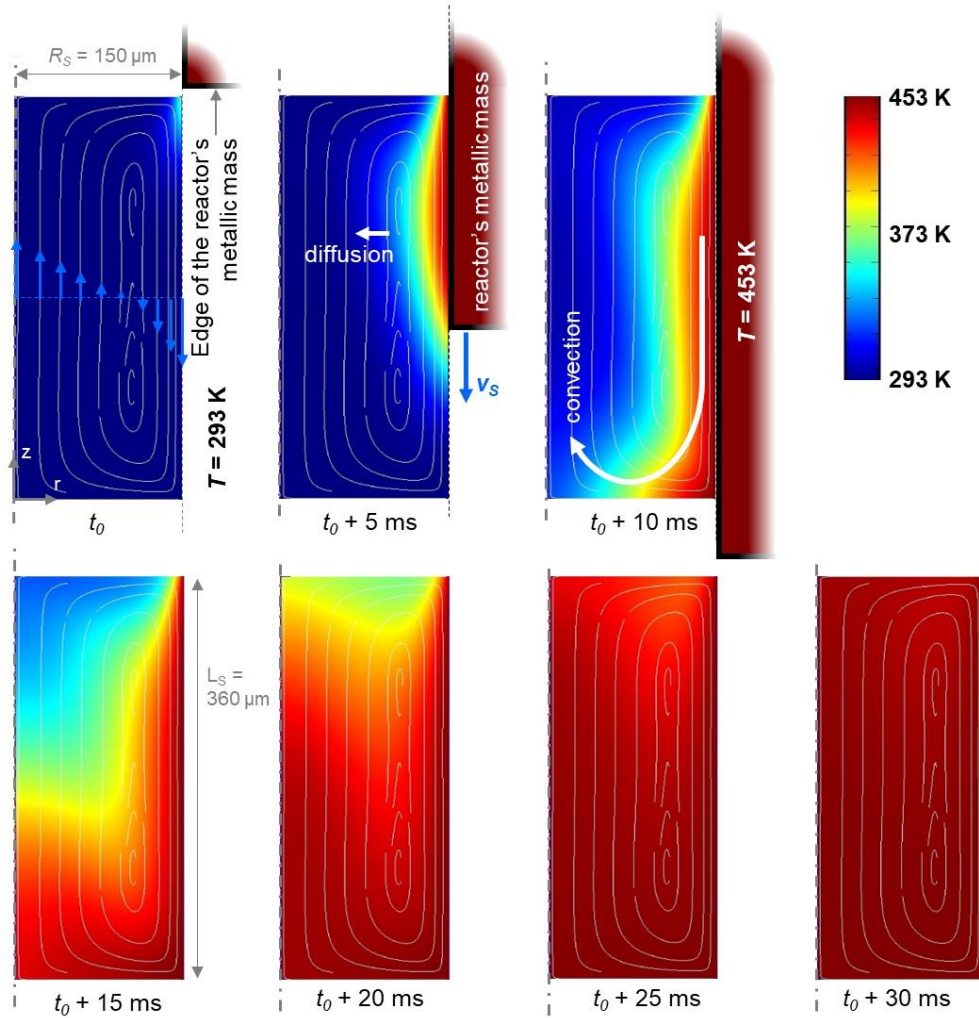
where  $L_S$  is the radius of the inner capillary (150 $\mu$ m),  $v_S$  is the lowest slug velocity (0.003m/s) and  $D_{glucose}$  was assumed to be the diffusivity of glucose in water (5.2 x 10<sup>-9</sup> m<sup>2</sup>/s).

$$Pe_H = \frac{L_S v_S}{\alpha} = 0.3 - 4.3$$

where  $R$  is the radius of the inner capillary (150 $\mu$ m),  $v_S$  is again the lowest slug velocity (0.003m/s) and  $\alpha$  was assumed to be the thermal diffusivity of water (1.4 x 10<sup>-7</sup> m<sup>2</sup>/s).

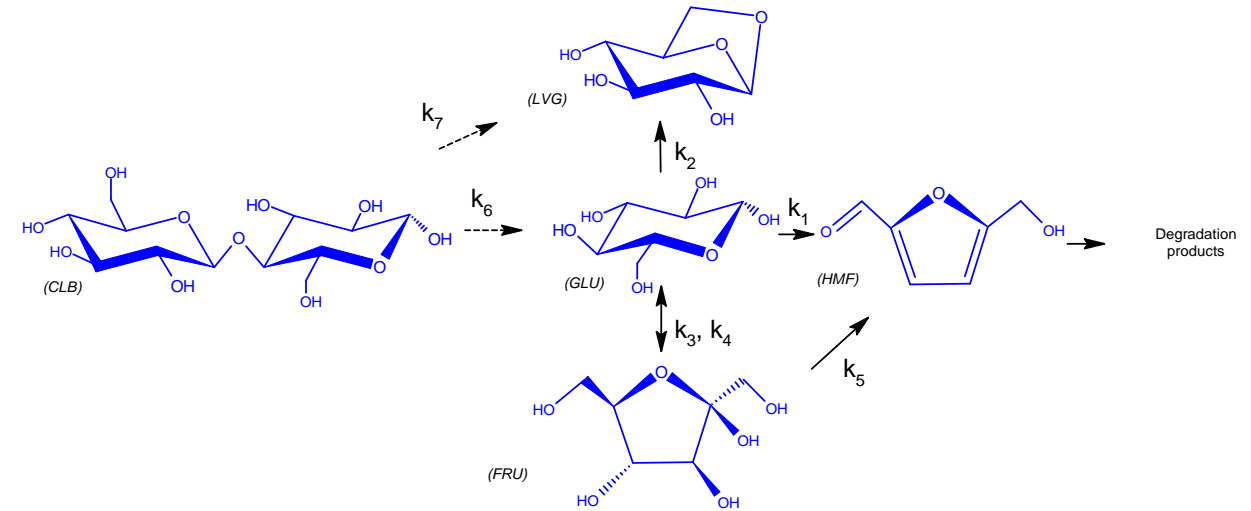
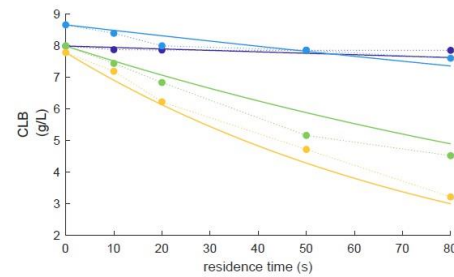
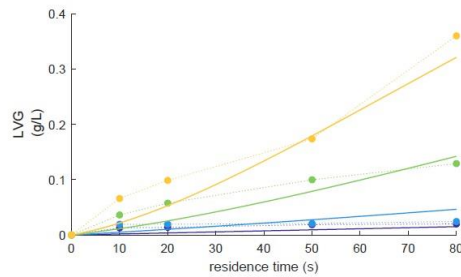
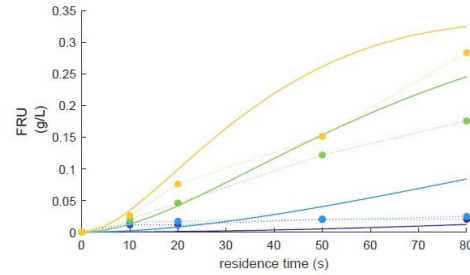
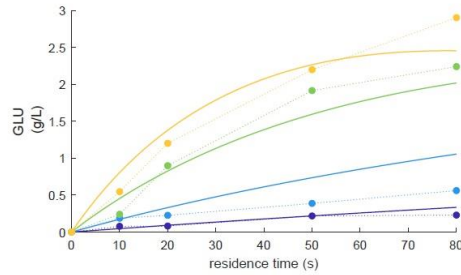


# Modélisation thermique et de l'hydrodynamique



721 - 5,333 K/s

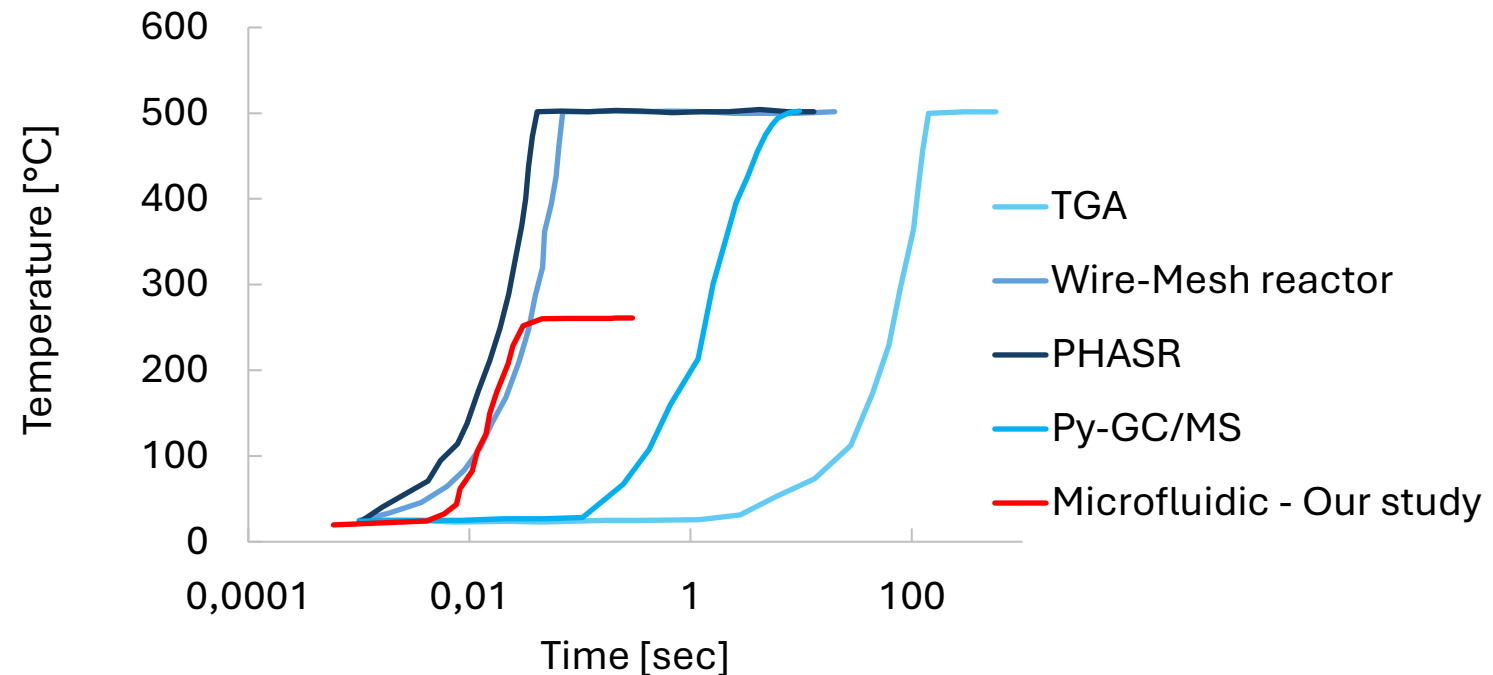
# Global kinetic modelling



	A (s <sup>-1</sup> )	E <sub>a</sub> (kJ/mol)
<b>GLU → HMF, dehydration, <math>k_1</math></b>	25784	71.6
GLU → LVG, dehydration, $k_2$	73071	88.2
GLU → FRU, isomerization, $k_3$	$6.4 \times 10^5$	66.5
FRU → GLU, isomerization, $k_4$	$5.3 \times 10^7$	75.8
<b>FRU → HMF, dehydration, <math>k_5</math></b>	713.71	40.4
<b>CLB → GLU, hydrolysis, <math>k_6</math></b>	$2.2 \times 10^5$	74.7
CLB → LVG, transglycosylation - dehydration, $k_7$	59.2	50.1

# Conclusions

- Develop methodologies capable of controlling kinetic regime and correcting system lags;
- Produce experimental datasets describing the reactivity of biomass under the kinetically controlled regime and non-isothermal and isothermal conditions;
- Associate measured macrokinetic parameters with model-fitting approaches to simulate the devolatilization stage of biomass fast pyrolysis and the ILC thermal behavior.



***Merci pour votre attention,***

***à tou.te.s les auteurs et autrices de ces travaux***

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Chrystel Auriol      Jean-Marie Sabathier      Pierre Bertorelle      Denis Marty      Mickael Ribeiro  
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