Modeling the influence of temperature on product distribution from biomass fast pyrolysis by the Monte Carlo method.

RAPSODEE UMR CNRS 5302
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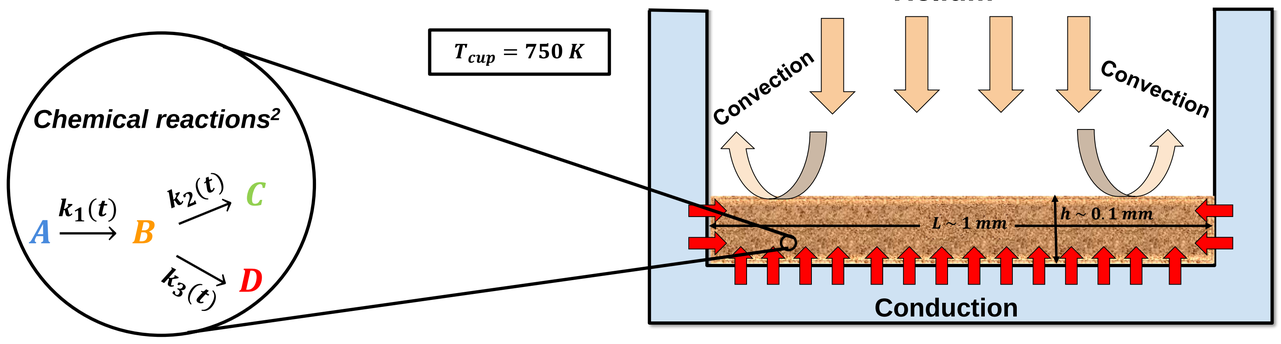
Background

- ***Bio-oil resulting from fast pyrolysis of biomass is considered as a valuable ressource of chemicals,***
- ***Process modelling requires to conduct biomass fast pyrolysis under kinetic-controlled regime.***[1]



Heat equation[1]

$$\partial_t\left(\rho_B C_p^B T\right) = \nabla.\left(-\lambda \nabla T\right) + Q_{rxn}(T)$$

$$T(t = t_0) = T_0$$

Objectives

- Study the effect of heat transfer on the distribution of pyrolytic products.
- Model pyrolysis kinetics of a biomass sample arrangement in a reactor by considering the thermal mechanisms of its environment and within it.
- Perform a thermal kinetic coupling in the system (reactor + biomass) through a formulation in path space and as nested expectations, using Monte Carlo simulation.

Illustration of Monte Carlo simulation

How to estimate the solution of a first order linear kinetic equation using Monte Carlo simulation ?

$$A \xrightarrow{k} B$$

From ODE to expectation formulation

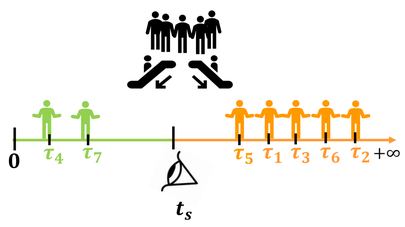
$$\begin{cases} \frac{dX_A}{dt} = -kX_A \\ X_A(t=0) = X_0 \end{cases}$$

$$X_A(t_s) = \int_0^{+\infty} f(\tau) \times p(\tau) d\tau \approx \sum_{i=1}^{N} \frac{\omega_i}{N}$$

$$f(\tau) = \begin{cases} X_0, & \tau \geq t_s \\ 0, & \tau < t_s \end{cases}, \qquad p(\tau) = ke^{-k\tau}$$

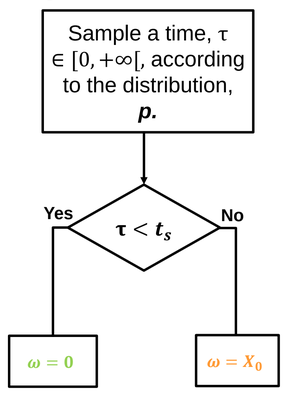
p is probability density function
ω_i is the associated weight with each realization
t_s is the probe point $[s]$

Illustration by random walkers



$$X_A(t_s) \simeq \frac{\Sigma\omega(🚶) + \Sigma\omega(🚶)}{\Sigma🚶 + \Sigma🚶}$$

Algorithmic illustration



Kinetic modeling

► **Degradation pathway: Transcription of a non-linear 1st order ODEs system into an expectation system**[3]

$$\begin{cases} \frac{dX_A(t)}{dt} = -k_1(t)X_A(t) \\ \frac{dX_B(t)}{dt} = k_1(t)X_A(t) - (k_2(t) + k_3(t))X_B(t) \\ \frac{dX_C(t)}{dt} = k_2(t)X_B(t) \\ \frac{dX_D(t)}{dt} = k_3(t)X_B(t) \end{cases} \quad k_2(t) + k_3(t) = k_s(t) \quad \Longleftrightarrow \quad \begin{cases} X_A(t) = \int_0^{+\infty} \tilde{k}_1 e^{-\tilde{k}_1\tau} d\tau \left(\mathcal{H}(t > \tau)\,[X_A(0)] + \mathcal{H}(t < \tau)[\frac{\tilde{k}_1 - k_1(t-\tau)}{\tilde{k}_1} X_A(t-\tau)]\right) \\ X_B(t) = \int_0^{+\infty} \tilde{k}_s e^{-\tilde{k}_s\tau} d\tau \begin{cases} [X_B(0)] & \mathcal{H}(t > \tau) \\ \left[\frac{k_1(t-\tau)}{\tilde{k}_s} X_A(t-\tau) + \frac{\tilde{k}_s - k_s(t-\tau)}{\tilde{k}_s} X_B(t-\tau)\right] & \mathcal{H}(t < \tau) \end{cases} \\ X_c(t) = \int_0^t \left[\frac{k_2(\tau)X_B(\tau)}{pdf_c(\tau)}\right] pdf_c(\tau) d\tau \\ X_D(t) = \int_0^t [\frac{k_3(\tau)X_B(\tau)}{pdf_D(\tau)}]\, pdf_D(\tau) d\tau \end{cases}$$

Arrhenius law[4], $k_j(T) = A_j e^{\frac{-E_{a,j}}{RT}}\ [s^{-1}]$
Upper bound of the reaction rate constant, k_j: $\tilde{k}_j$[5] $[s^{-1}]$

$$\forall i \in \{A, B, C \text{ or } D\}\ X_i(t) = \mathbb{E}\left(W(\tau)\right) \simeq \frac{1}{N} \sum_{k=0}^{N} \omega(\tau_k)$$

Thermal modeling

► **Heat equation: Thin and non-reactive biomass film**[1]

$$V_B \rho_B C_p^B \frac{dT}{dt} = -U_{ext}\left(T - T_{cup}\right) S_B$$

$$\begin{cases} T(t = t_0) = T_0 & = 293.15\ K \\ T_{cup} & = 750\ K \end{cases}$$

► **Analytical solution:**

$$T(t) = T_{cup} + \left(T_0 - T_{cup}\right) e^{-\gamma(t - t_0)}$$

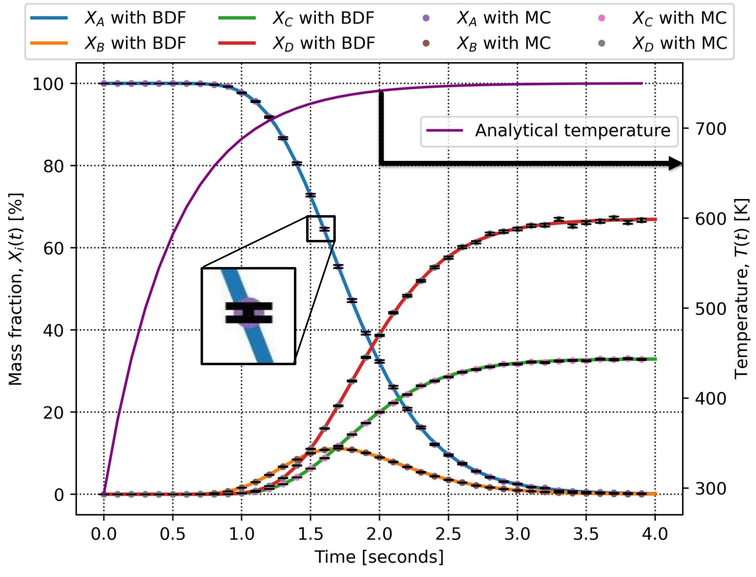
$$\gamma = \frac{S_B U_{ext}}{V_B \rho_B C_p^B}$$

C_p^B	$[J.K^{-1}.kg^{-1}]$
ρ_B	$[kg.m^{-3}]$
V_B	$[m^3]$
S_B	$[m^3]$
U_{ext}	$[W.m^{-2}.K^{-1}]$
γ	$[s^{-1}]$

$$Py^{II} = \frac{k}{\gamma} \sim 10^2 - 10^4$$

Results and Conclusions

All calculations were performed with a sample size of $N = 10^4$



BDF[6]: Backward Differentiation Formula

MC: Monte Carlo

- Monte Carlo Integral Formulation can solve a system of non-linear 1st order ODEs and by default a system of linear 1st order ODEs .
- It is possible to estimate mass fraction or molar fraction via several and independent probe points calculations (Each point showed in the figure above).
- Thermal/kinetic coupling can be treated in the case of prescribed thermal model.

Perspectives

- Working on complex degradation pathways related to the lumped or detailed models representing pyrolysis kinetics.
- Treating stiffness that represents one of the most challenging properties of chemical systems.
- Studying the thermal/kinetic coupling with the non-reactive biomass in zero-dimension, or by considering the internal diffusion, and the reactive biomass model via a single Monte Carlo algorithm.

Other institutions

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References

1. Manel Nasfi *et al.* Journal of Analytical and Applied Pyrolysis. V 165, August 2022, 105582, doi: 10.1016/j.jaap.2022.105582

2. Eliseo Ranzi *et al.* ACS Sustainable Chem. Eng. 2017, 5, 4, 2882–2896, doi: 10.1021/acssuschemeng.6b03098

3. Mouna El Hafi *et al.* Journal of Quantitative Spectroscopy and Radiative Transfer. Volume 260, February 2021, 107402, doi: 10.1016/j.jqsrt.2020.107402

4. Sergey Vyazovkin *et al*. Thermochimica Acta. Volume 520, Issues 1–2, 2011,Pages 1–19, doi:10.1016/j.tca.2011.03.034

5. Yaniss Nyffenegger-Péré *et al.* J. Phys. Chem. A 2023, 127, 8, 1988–1997, doi: 10.1021/acs.jpca.2c06893.

6. Robert K. Brayton *et al.* Proceedings of the IEEE, vol. 60, no. 1, pp. 98-108, Jan. 1972, doi: 10.1109/PROC.1972.8562.

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