

Investigation of heat transfer limitations in the Micropyrolyzer during biomass fast pyrolysis

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1. Introduction

Many conflicting mechanisms and diverse kinetics models have been proposed to underly the chemistry of biomass decomposition, making the fundamental science of biomass pyrolysis lacking models capable of describing the chemistry and transport in industrial reactors.

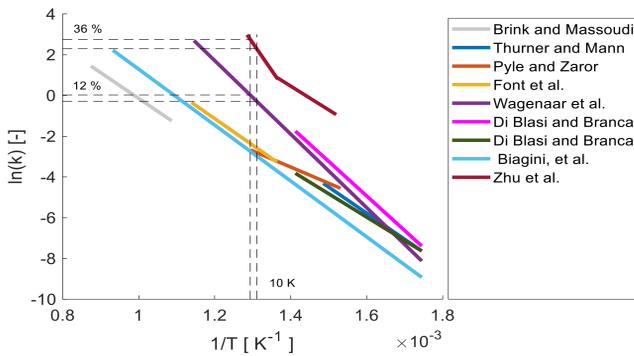


Fig. 1. Arrhenius plot for biomass pyrolysis

Commercial analytical pyrolysis systems have become increasingly used in biomass fast pyrolysis research. Establishing experimental conditions free from heat transfer limitations using these micro-reactors has not been verified. Since accurate measurement of biomass sample temperature with these devices is not possible, the isothermal character of experiments has also never been verified.

2. Goals of the study

- Establish the typical operating conditions to conduct kinetics in the absence of heat transfer limitations within the micropyrolyzer.
- Verify the isothermal character of biomass fast pyrolysis.

3. Methodology

Dimensional analysis

$$Biot = \frac{\tau_{conduction}}{\tau_{external\ heat}} = \frac{U L}{\lambda}$$

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

$$Py' = \frac{\tau_{reaction}}{\tau_{external\ heat}} = \frac{U}{c_p L k \rho}$$

Thermal model

Governing equations: Navier Stokes equations (compressible fluid and laminar flow); Energy equation; Stefan-Boltzman law.

Boundary conditions:

- Internal surfaces (IS): Continuity of temperature and energy flux; No slip (IS of the reactor); Diffuse gray surfaces (IS of the cup, $\epsilon = 0.32$, IS of the Quartz tube, $\epsilon = 0.93$).

- Outer surfaces (OS): Diffuse gray surfaces (OS of the heating sleeve, $\epsilon = 0.32$, OS of the support, $\epsilon = 0.8$, OS of the cup, $\epsilon = 0.32$, OS of the Quartz tube, $\epsilon = 0.93$, OS of the biomass sample, $\epsilon = 0.9$; Insulation (OS of the insulator).

- Inlet and outlet Helium: Inlet Helium : $v = 0.12$ m/s, outlet Helium: $P = 2.9$ bar.

Simulation: COMSOL Multiphysics® v5.5

Validation: Temperature measurements using a thermocouple (type K and 0.25 mm in diameter; TC S.A.) connected to the Agilent 34970A acquisition unit.

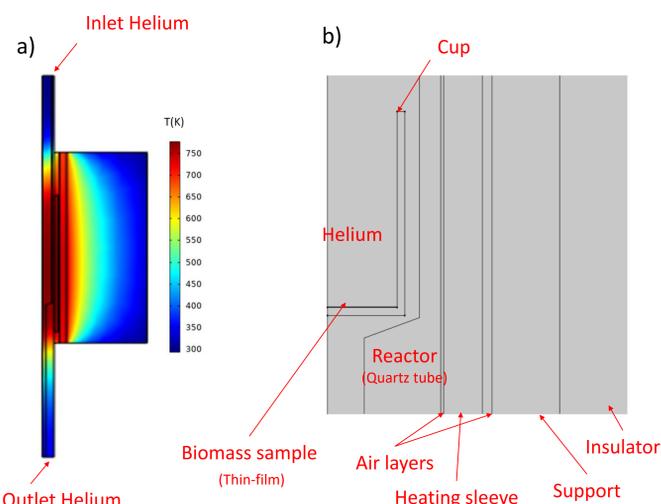


Fig. 2. Components of the micropyrolyzer as described in the simulation.

4. Results

4.1. Temperature-time evolution of the cup

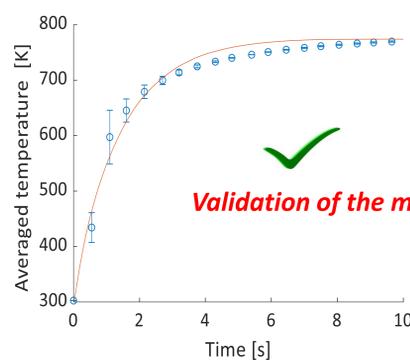


Fig. 3. T-t evolution of the cup : simulated (continuous line) and measured (circles) in the micropyrolyzer at 500 °C.

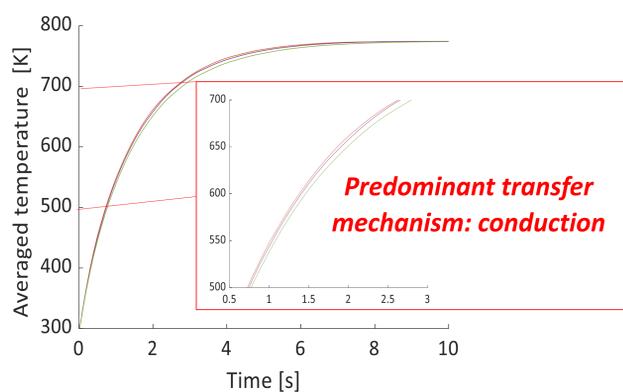


Fig. 4. Simulated T-t of the cup at 500°C according to heat transfer mechanisms: conduction, conduction + convection, conduction + convection + radiation.

4.2. Heating of samples

Powdered biomass arranged according to extreme configurations:

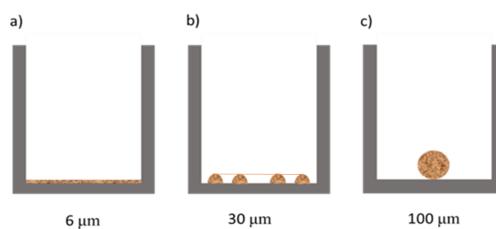


Fig. 5. 50 μg of biomass powder ($\rho_{biomasse} = 409$ kg/m³): a) Thin-film, b) torus, and c) sphere.

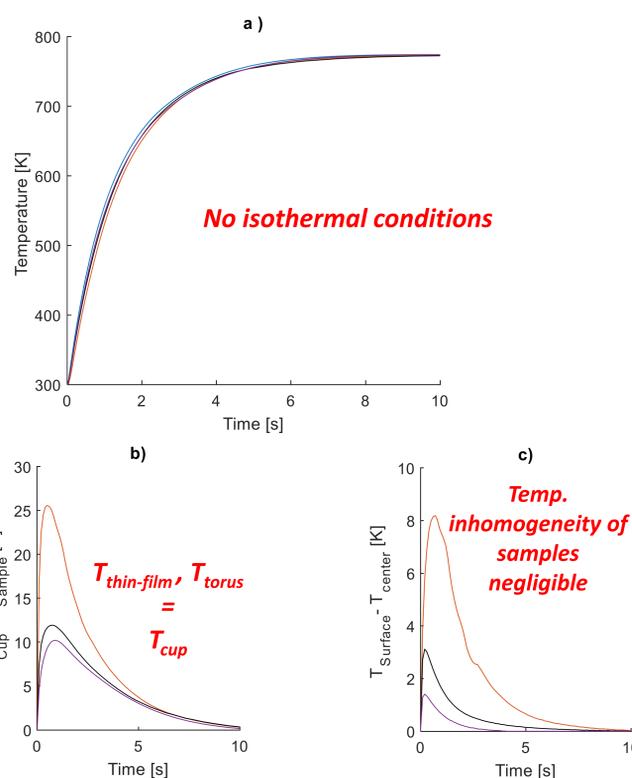


Fig. 6. Heating of biomass samples at 500 °C: (a) T-t histories of the cup and biomass samples (sphere, torus, and thin-film). Comparison between (b) cup and samples averaged temperatures and (c) surface and center temperatures of samples.

Acknowledgements

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4.3. Temperature profile & reaction rate

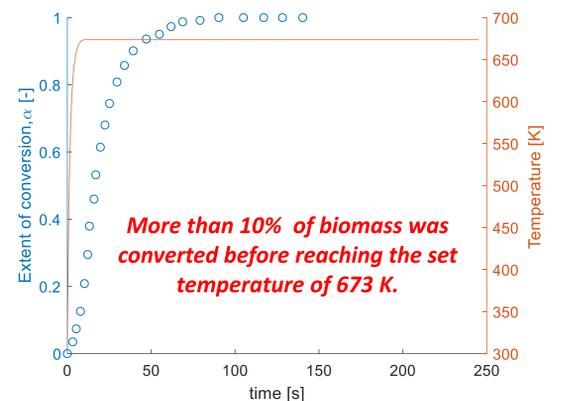


Fig. 7. Conversion curve for cellulose thermal decomposition using the Frontier lab micropyrolyzer at 400 °C [1]. Simulated temperature history of biomass sample (torus conf.) in the same conditions.

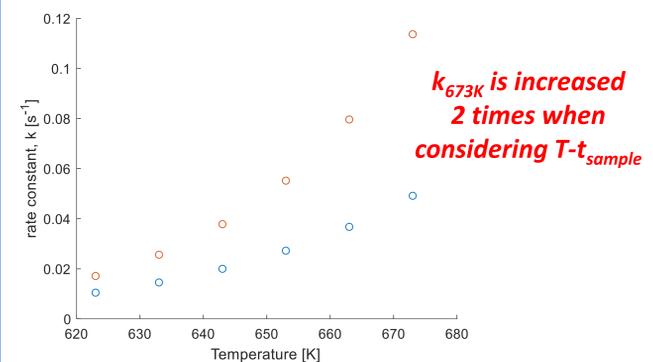


Fig. 8. Direct plots of cellulose thermal decomposition under isothermal and non-isothermal conditions.

4.4. Pyrolysis regime

Calculated heat transfer coefficients = 165 - 244 W.m⁻².K⁻¹ for different sample arrangements and between 623 to 773 K.

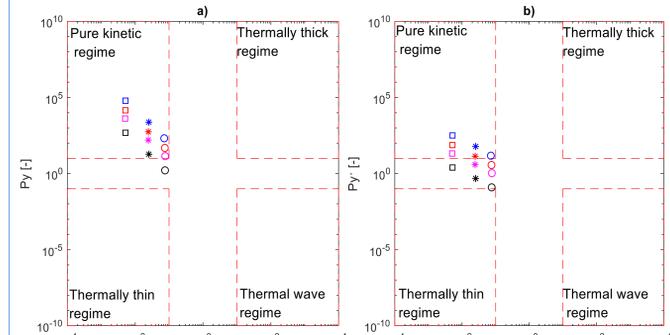


Fig. 9. Reaction-transport map for biomass fast pyrolysis: 50 μg arranged as thin-film (□), torus (*), sphere (o) at 623 K, 673 K, 723 K, and 773 K. a) Py vs. Bi and b) Py' vs. Bi . Woody biomass thermophysical properties were used.

Intrinsic kinetic conditions for thin-film and torus between 623-773 K

5. Conclusions

- Micropyrolyzer kinetics of biomass fast pyrolysis can be carried out without heat transfer limitations by using small masses of biomass (≤ 50 μg) carefully arranged in thin-film;
- For $T > 450$ °C, the reaction is so fast that the pure kinetic regime cannot be maintained;
- The heating time of biomass was significant, indicating the non-isothermal nature of the experiment;
- Kinetics analysis requires establishing the biomass sample temperature history;
- The most predominant transfer mechanism in the micropyrolyzer is conduction.

Reference

[1] N. Phusunti, A. Hornung, Formal Kinetic Parameters – Problems and Solutions in Deriving Proper Values, (2014) 257–284.

Nomenclature

τ : time scale of reaction or conduction or external heat (s)
 U : overall external heat transfer coefficient (W/m²K)
 k : apparent kinetic rate constant (s⁻¹)
 λ : thermal conductivity of the biomass sample (W/m K)
 C_p : heat capacity of the biomass sample (J/kg K)
 L : characteristic length of the biomass sample (m)
 ρ : density of the biomass sample (kg/m³)
 ϵ : emissivity