

# Development of a kinetic scheme for biomass pyrolysis with detailed description of volatiles: a combined experimental and modeling strategy

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## Highlights

- A novel TGA-based methodology allows complete speciation of pyrolysis products.
- Distinct kinetics and products from cellulose, xylan and glucomannan are revealed.
- A scheme of biomass pyrolysis with refined description of volatiles is developed.

## 1. Introduction

Pyrolysis of lignocellulosic biomass represents a promising solution to generate liquid biofuels that can help the decarbonization of critical sectors, such as aviation and marine markets. However, the complex multi-component and multi-phase nature of the process has hindered the obtainment of rigorous experimental data on biomass devolatilization, necessary for the refinement of kinetic schemes and technology optimization [1]. This study proposes a combined experimental and modeling strategy for the development of lumped kinetic schemes of biomass pyrolysis with detailed description of volatiles. Cellulose and two hemicelluloses – hardwood xylan and softwood glucomannan – have been investigated.

## 2. Methods

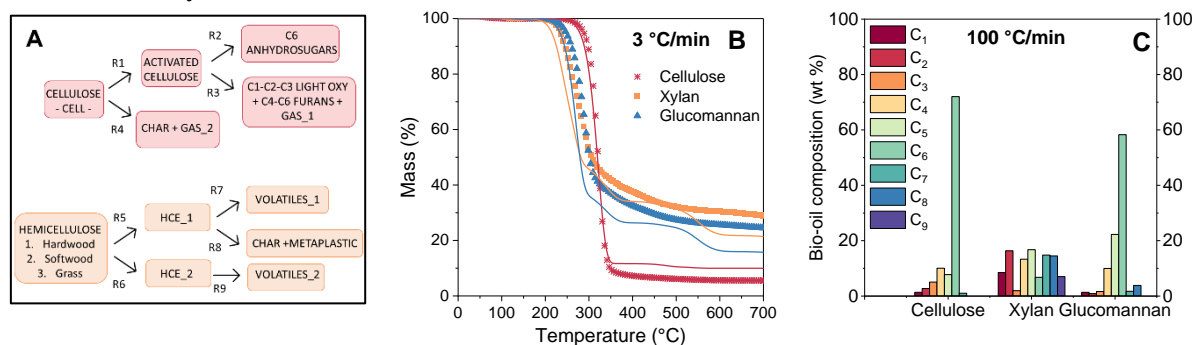
Pyrolysis tests are run in a thermogravimetric analyzer (TGA), subjecting biomass samples to a controlled heating ramp (3-100 °C/min), under He flow (85-275 NmL/min). Different analytical techniques and sampling protocols are employed to quantify the diverse classes of pyrolysis products. The solid residual is measured by TGA micro-balance. Heavy oxygenates are captured in commercial sorbing tubes (ORBO 609) during experiments and integral composition analyses are performed in an offline GC-MS/FID. Light oxygenates are sampled with a gas syringe during pyrolysis tests and offline analyses are performed in GC-MS/FID. Gases and H<sub>2</sub>O flowrates are monitored during pyrolysis tests in an online mass spectrometer. The combination of these multiple analytical techniques and calibration protocols allow to determine the integral mass yield of each compound.

The lumped kinetic scheme proposed by Debiagi et al. [2] is employed for the simulations of cellulose and hemicellulose pyrolysis. This is a semi-empirical model, that uses lumped reactions and lumped species to describe the devolatilization of biomass and product distribution. Fig.1a shows the kinetic scheme, composed of 4 lumped reactions for cellulose devolatilization (R1-R4) and 5 lumped reactions for hemicellulose devolatilization (R5-R10). Apparent first-order rate laws are used. Simulations are performed in OpenSMOKE++, a versatile framework for numerical simulations of reacting systems [3].

## 3. Results and discussion

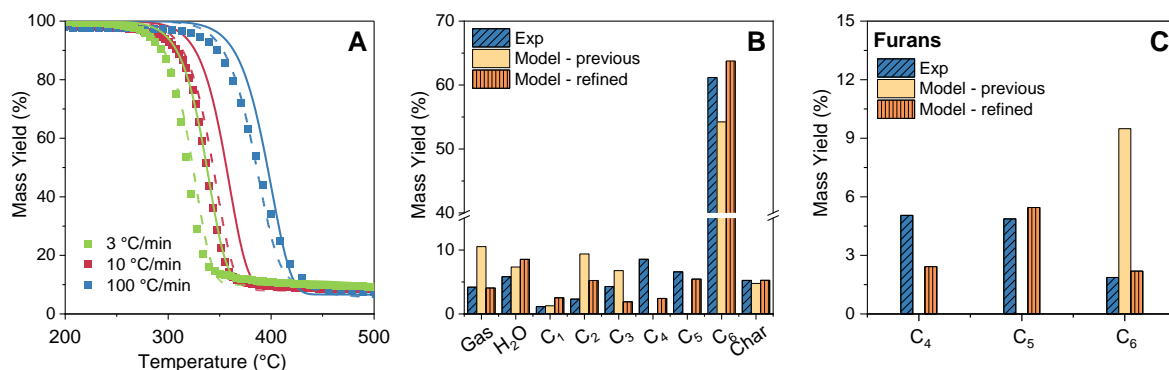
Fig.1b and Fig.1c show devolatilization trends and product distribution measured for cellulose, xylan and glucomannan. The effect of temperature is studied by performing experiments at varying heating rate, and more than 45 products are identified and individually quantified, reaching impressive mass balances above 90%, a notable achievement in particular for xylan and glucomannan that are scarcely studied in the literature. Peculiar features for each biomass emerge, in terms of both devolatilization kinetics and product distribution, highlighting the crucial importance of independent studies on these macro-constituents. In cellulose pyrolysis, the bio-oil yield is maximized, with the prevalence of the C<sub>6</sub> anhydrosugar levoglucosan. Xylan products are almost evenly distributed among the solid, liquid and

gas streams. Glucmannan, with its hybrid chemical structure, displays a behavior intermediate between cellulose and xylan.



**Figure 1.** a) Lumped pyrolysis model; b) TG curves (exp = symbols; model = lines) and c) experimental bio-oil composition from cellulose and hemicellulose.

Fig.2 displays the comparison between new cellulose pyrolysis data and model predictions. The previous model exhibits significant discrepancy in the description of volatiles, in particular among C<sub>2</sub>-C<sub>5</sub> oxygenates. The new experimental findings are used to develop a refined kinetic scheme with new reactions and new lumped species, aiming to provide an improved description of volatile species. The refinement of the model has involved a partial de-lumping of products: a new pseudo-species is added to account for anhydrosugars that are not levoglucosan, and species FURAN and FURFURAL are introduced to represent C<sub>4</sub> and C<sub>5</sub> products, which were absent in the previous version. The comparison with refined model predictions demonstrates a notable enhancement, both in terms of devolatilization trends (Fig.2a) and products description (Fig.2b-c). The model has been validated with further literature data. Ongoing activities focus on developing a refined model for xylan and glucmannan.



**Figure 2.** Comparison between experiments and model predictions of cellulose pyrolysis. (a) TG curves: exp = symbols; previous model = solid lines; refined model = dashed lines; (b-c) yields of products at 100 °C/min.

#### 4. Conclusions

A combined experimental-modeling strategy for the development of kinetic schemes of biomass pyrolysis is presented, based on a TGA-setup and a semi-detailed lumped kinetic scheme. This experimental setup has proven a flexible and unique solution for the comprehension of biomass devolatilization chemistry and tuning of kinetic schemes, necessary for the progress of technology.

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#### Keywords

Biomass pyrolysis; kinetic modelling; detailed speciation; TGA.