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Executive Summary of the Thesis

Experimental investigation on biomass pyrolysis: the case studies of rice husk and physical mixtures of model components

Laurea Magistrale in Eneergy Engineering - Ingegneria Energetica

Author: Alessandro Guarnieri

Advisor: Prof. Alessandra Beretta

Co-advisor: Veronica Piazza, Eleonora Benedetto

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1. Introduction

In the current energy transition scenario, the necessity of reducing CO_2 emissions has driven the growing interest towards potential sustainable fuels. Among other alternatives, lignocellulosic biomass stands out as a promising solution because of its widespread availability, dispatchability and versatility, making it an appealing feedstock for the production of biofuels and sustainable chemicals. The focus of this thesis work is directed towards lignocellulosic biomass pyrolysis, the thermochemical conversion process which is able to decompose in a non-selective way complex biomass components. When heated in a controlled way in an inert atmosphere, biomass generates three streams of products (a solid carbon rich char, liquid bio-oil and gaseous compounds) with valuable chemical nature and energy content. Lignocellulosic biomass is composed by three main constituents: cellulose, hemicellulose and lignin. Previous studies on the pyrolysis of these macro-constituents have identified cellulose, a regular C6 polymer, as the major source of bio-oil, with levoglucosan as the main product. [1] On the other hand, hemicellulose, characterized by a branched chemical structure made of C5-C6 sugars, and lignin, an aromatic matrix which adds strength and rigidity to the plant cell walls, were found to be the primary source of carbon oxides (CO and CO_2) and bio-char, respectively. [2, 3] However, while literature provides a broad experience on the pyrolysis of single components, studies on the decomposition behaviour of complex feedstocks, such as real biomasses and physical mixtures of model components, and on the interaction of their constituents are still at an early stage, often with contradictory conclusions.

Given these premises the present study initially focused on the pyrolysis of rice husk, a byproduct of rice milling which is commonly found in Northern Italy [4], investigated through Thermogravimetric Analysis (TGA). Additionally, the qualitative and quantitative speciation of pyrolysis products was achieved by means of Mass Spectrometry (MS) and Gas Chromatography (GC). Then, the research explored the possibility of reconstructing the pyrolysis behaviour of rice husk with the hypothesis of additivity of its macro-constituents, which is a key assumption in the study of lumped kinetic models. [5] Devolatilization trends and

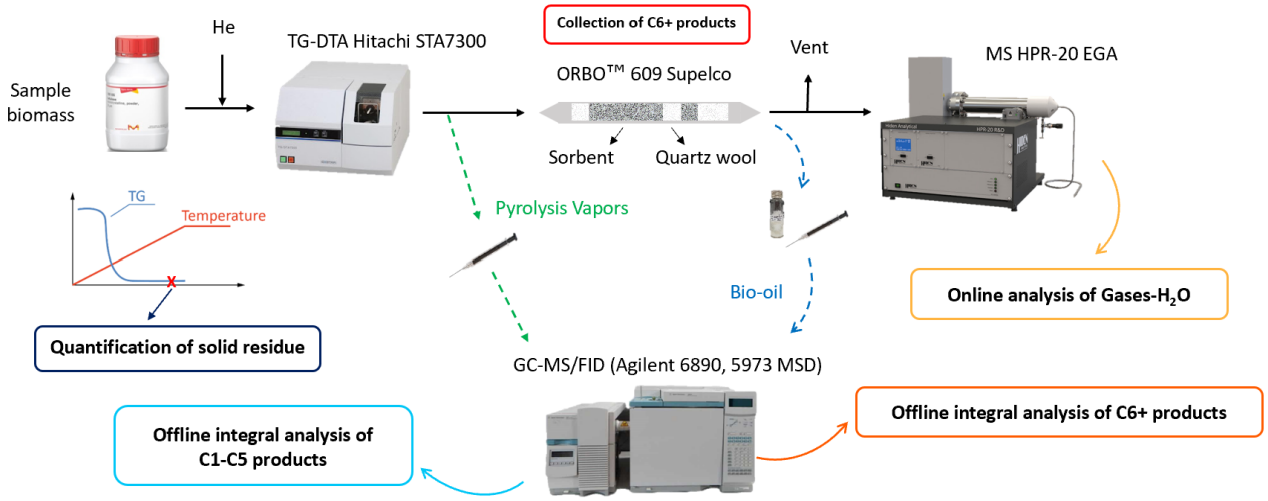

Figure 1: TGA-based experimental setup for kinetic investigation, adapted from [1]

products' yields of rice husk pyrolysis were predicted from the weighted contributions of its main components (cellulose, hemicellulose, lignin), without accounting for interactions. Finally, physical mixtures (cellulose-lignin and xylan-lignin) of commercial powders were also tested and the results were compared with the expected outcome of non-interacting chemical behaviour to better identify potential synergistic effects in complex biomass feedstocks.

2. Matherials and experimental procedures

The rice husk sample investigated in the experimental campaign was provided by Riseria de Medici, Trecate (NO), while commercial powders for the preparation of physical mixtures of model components were purchased from Sigma-Aldrich, in the case of cellulose and alkali lignin, and from Megazyme for beechwood-derived xylan, which was considered to be representative of the thermal behaviour of hemicellulose. To perform the experiments, a pre-existing experimental setup (*Figure 1*) was employed. Pyrolysis analysis was conducted in a thermogravimetric analyser (TGA), model Hitachi STA7300 TG-DTA, following a four-step process. The sample is initially kept at ambient temperature for 40 min with a continuous He flow of 270 Nml/min to create an inert environment, then, a linear temperature increase at 50°C/min up to 150°C allows to dry the biomass sample. Subsequently, the reaction chamber is heated at 10, 20, 50 or 100°C/min until 950°C to perform pyrolysis. Ultimately, a 10-min hold at 950°C flushing an air flow rate of 200 Nml/min is employed to burn residual char and volatile products. The TGA software provides data in the form of percentage mass loss (TG) and its derivative against time (DTG), displayed as functions of time and sample temperature. By examining these, the thermal behaviour of the sample and its devolatilization rate were assessed. Regarding the quantification of pyrolysis products, the online analysis of gaseous species (H_2, CH_4, H_2O, CO and CO_2) was performed by means of a mass spectrometer (MS), model HPR-20 EGA by Hiden Analytical, connected to the outlet section of the TGA, while the offline integral analysis of light (C1-C5) and heavy (C6+) condensable compounds was achieved inside a gas chromatograph (GC), model GC-6890 by Agilent. The GC product analysis relied on two distinct procedures. Pyrolysis vapours were directly sampled from a dedicated sampling point at the outlet of the TGA and promptly injected into the GC using a gas syringe. Differently, heavier condensable compounds were retained inside a commercial sorbing trap, the Orbo™ 609 trap, during the entire duration of the pyrolytic process. Afterwards, the sorbing material was transferred into a vial and washed with a 10 ml solution of acetone and fluoronaphthalene, which is used as internal standard for data processing. After extraction of the collected

compounds, a 2 μl sample was tested inside the GC. Here, chemical species were identified by the GC-MS detector, which matches each peak of the chromatogram to a specific compound, while their concentration was quantitively estimated by the GC-FID detector. To improve the GC analysis, the sampling of condensable products was performed considering a reduced He flow rate, i.e. 130 Nml/min, and a heating rate of 100°C/min in the TGA.

The additive reconstruction of pyrolytic behaviour (TG and DTG curves) and products' yields was obtained from the weighted contribution of individual components of the sample as in *Equation* (1), starting from experimental data.

$$\begin{cases} TG_{theo} = \sum_{i=1}^{n} TG_i \cdot x_i \\ DTG_{theo} = \sum_{i=1}^{n} DTG_i \cdot x_i \\ yield_{theo} = \sum_{i=1}^{n} yield_i \cdot x_i \end{cases} \quad (1)$$

3. Results and discussion

In this section, relevant findings of the experimental campaign conducted on complex biomass feedstocks, i.e. rice husk and physical mixtures of model components, are presented and the applicability of the additive reconstruction is assessed.

3.1. Rice husk pyrolysis

Testing a real biomass led to unprecedented technical challenges, thus it required a tuning phase of the sample preparation procedure. The limited volume of the TGA crucible revealed to be an obstacle when studying rice husk in "as received" conditions. Consequently, the sample was grinded to improve its manageability and to test higher amounts. Additional experiments were performed to disregard the effect of He flow rate and sample mass.

Rice husk (RH) pyrolysis experiments were carried out considering 13 mg of initial weight and 270 Nml/min of continuous flow of He at different heating rates (10, 20, 50 and 100°C/min). TG and DTG curves are shown in *Figure 2*. The evaluation of the TG curve against the sample temperature has shown that mass loss occurs in a wide temperature range (150-700°C) and the solid residue accounted for 31.08% on dry mass basis at 10°C/min. On the other hand, from the DTG curve, in which every peak represents a devolatilization event, a complex and multi-event pathway was observed, with main contributions in terms of devolatilization rate detected between 250-400°C. The reason of such behaviour is to be attributed to the heterogenous nature of the feedstock. As it is visible in *Figure 2*, increasing the heating rate consistently shifted the onset temperature towards higher values and increased the intensity of the devolatilization peaks as a consequence of the accelerated conversion of the sample. Interestingly, no trend was found regarding the quantification of the solid residue for which the effect of the heating rate was limited.

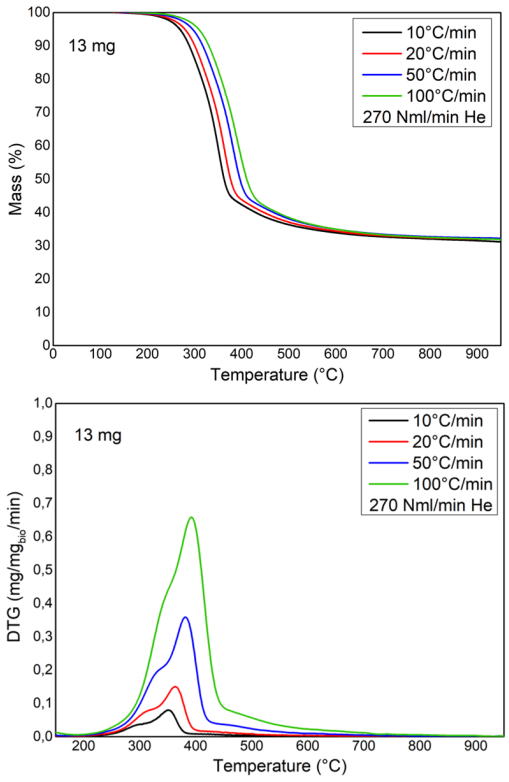

Figure 2: TG and DTG curves of RH at varying heating rate

A further step in the comprehension of rice husk pyrolysis was accomplished via products' speciation. A mass balance closure of 82.72% was achieved considering a heating rate of 100°C/min. *Figure 3* displays an overview of the mass yields of collected pyrolysis products grouped into solid residue, bio-oil, water and gases (CH_4, CO and CO_2), which accounted for 31.77%, 24.99%, 10.94% and 15.01% respectively. Regarding gas production, CO (5.29%) and CO_2 (8.46%) represented the largest fractions, while C6 sugars (5.31%) and phenolic derivatives (5.72%) were noticeable contributions of bio-oil. The non-finalization of the closure of the mass balance is due to technical challenges encountered in the analysis of bio-oil, with the expected fraction accounting for 42.27% instead of the quantified 24.99%. Nevertheless, the speciation is considered to be representative.

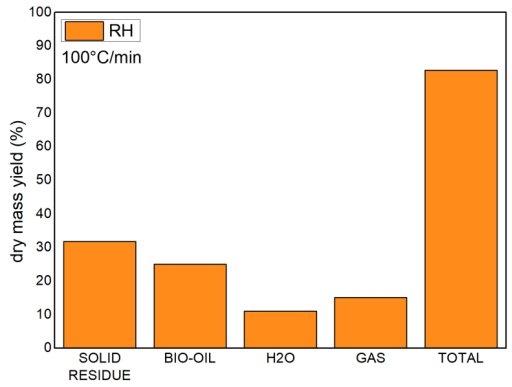

Figure 3: RH, pyrolysis products at 100°C/min heating rate

After the experimental verification of the real biomass reactivity, a virtual reconstruction of the global pyrolysis behaviour of the individual components (cellulose, xylan, glucomannan, arabinoxylan and lignin) weighted according to their mass fraction in the real sample (refer to *Equation* (1)) was obtained with the hypothesis of additivity of chemical contributions, that is under assumption of no chemical interaction. At this scope, the composition of the sample was internally characterised with a sequential fractionation procedure adapted from Allegretti et al. [6], which involved successive water and acid treatments. The outcome is reported in *Table 1*.

	[wt%]
soluble fraction	7.0
cellulose	35.0
hemicellulose	18.0
lignin	31.5
inorganic residue	8.5

Table 1: Macro-constituents of rice husk sample

The comparison between predicted TG and DTG curves of the reconstructed system of components (solid red line, theoretical RH), those of the reference individual macro-constituents (dashed lines) and the experimental curves from the real rice husk (solid black line) is shown in *Figure 4*, at the heating rate of 100°C/min. As it is observable, experimental and theoretical curves are almost superimposed for the entire temperature range, with a slight overestimation of the devolatilization peak at 375°C. Moreover, the onset temperature and the solid residue are well predicted by the theoretical reconstruction. Similar conclusions can be drawn from the comparison of integral mass yields as reported in *Figure 5*. From a general standpoint, the additive reconstruction was able to predict the overall distribution of pyrolytic products of rice husk. Water and gases was slightly overestimated, while the yield of solid residue and expected volatile species, computed as the closure of the mass balance, was moderately underestimated. Hence, no evidence of a strong chemical interaction between cellulose, hemicellulose and lignin was found.

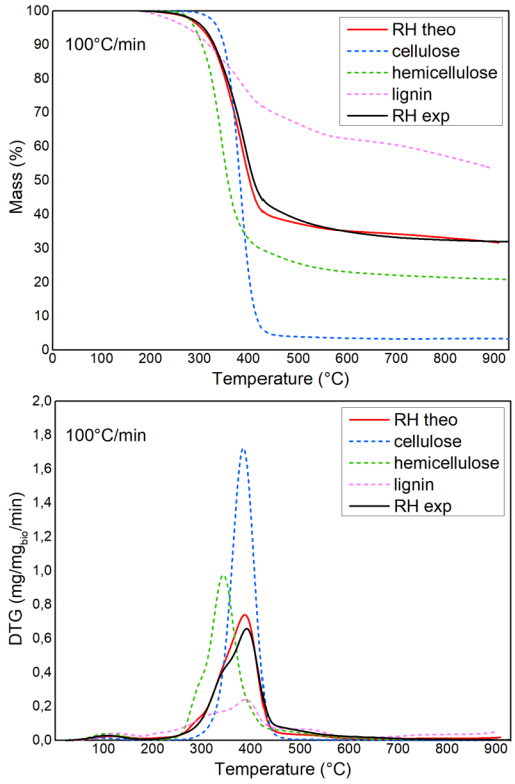

Figure 4: RH, comparison with additive reconstruction at 100°C/min heating rate

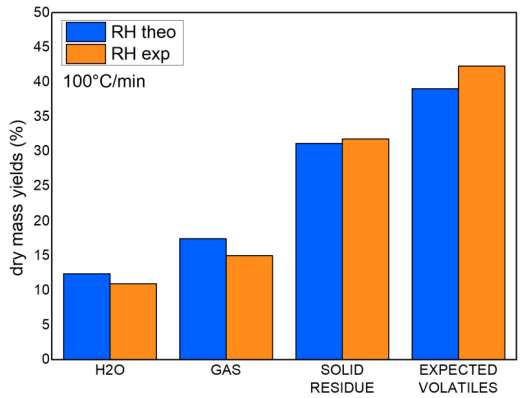

Figure 5: RH speciation, comparison with additive reconstruction

3.2. Physical mixtures pyrolysis

To corroborate the good adherence observed between experimental and simulated rice husk, a study on the pyrolysis of physical mixtures of model components was conducted. A common assumption in the study of lumped kinetic models of the pyrolysis of biomass is the independent decomposition of its macro-constituents. [5] In literature, the applicability of this hypothesis has been assessed by experimentally evaluating the pyrolysis of physical mixtures of model components (cellulose, hemicellulose, lignin), with contradictory conclusions. [7]

Binary cellulose-lignin system. *Figure 6* plots the TG and DTG curves of the cellulose-lignin mixture (50/50 wt%) at the heating rate of 10°C/min. From the DTG plot, it can be noted how the real mixture shows a peak which is reduced in intensity, delayed and enlarged in the temperature range of cellulose devolatilization (300-400°C). This difference results in the underestimation of the prediction of the solid residue and the overestimation of the expected fraction of condensable species.

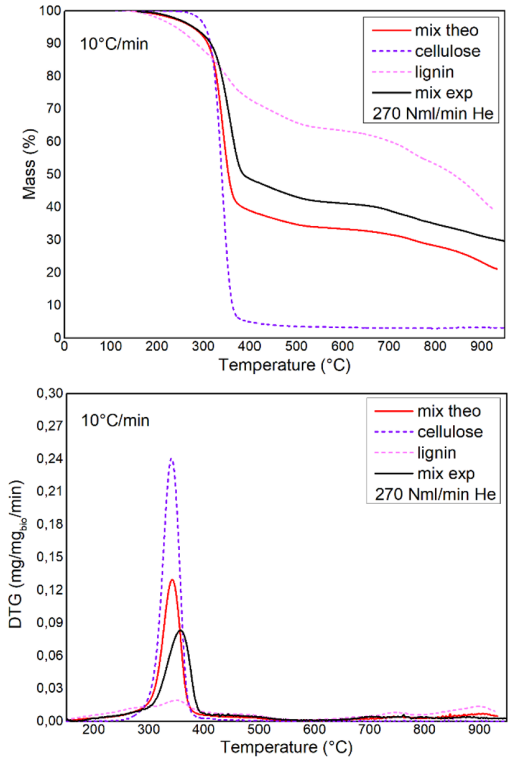

Figure 6: TG and DTG curves of cellulose-lignin mixture at 10°C/min heating rate

This behaviour was similarly detected also in the experiments conducted at 20, 50 and 100°C/min. Apparently, thus, the pyrolysis experiments with the physical mixtures reveal the presence of interactions, that were instead non detected in the real biomass.

Comparable observations were made by S. Stefanidis et al. [7] on the pyrolysis of the physical mixture cellulose-xylan-lignin performed in a

TGA at a heating rate of 10°C/min. The cause of the delay, reduction and enlargement of the main devolatilization peak was suggested to be the early decomposition of xylan and lignin, which start to decompose at low temperatures forming a charred film around the cellulose particles hence hindering heat and mass transfer.

To better investigate the origin of the observed effects and in particular to better understand whether the way in which the powders are contacted can affect the final response of the system, additional experiments were performed on a cellulose-lignin system where an attempt to physically segregate the components (no mixing) was obtained by layering the two macrocomponents in the TG crucible. *Figure 7* reports the TG and DTG curves of the configuration with a layer of cellulose powders on top of lignin powders. As it can be seen, this resulted in an improvement of the adherence to theoretical results compared to the case of the intimate mixture (*Figure 6*), thus suggesting that the physical contact between the components might be the cause of the previously observed discrepancy.

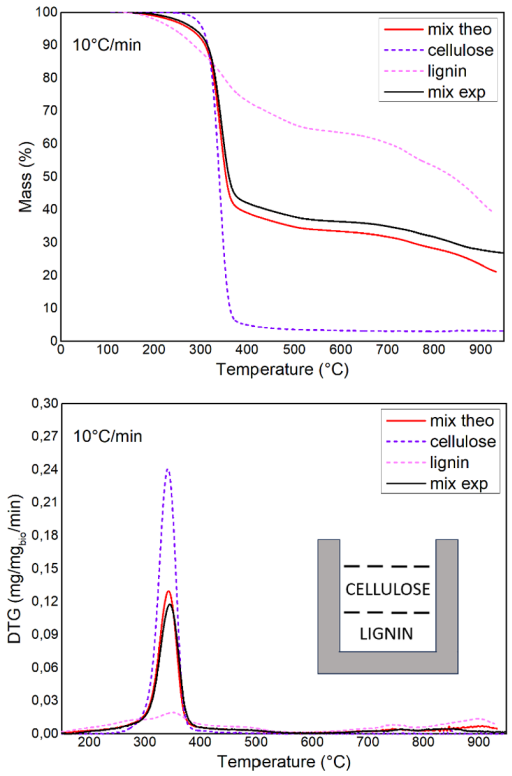

Figure 7: Cellulose-lignin mixture, different mixing degree at 10°C/min heating rate

Binary xylan-lignin system. The chemical behaviour of the binary xylan-lignin system (50/50 wt%) was also tested and *Figure 8* reports the comparison between experimental and theoretical TG curves at the heating rate of 20°C/min. From TG curves a moderate deviation from the behaviour of the non-interacting mixture (theoretical mixture) is detected, with the experimental system showing a slighlty higher solid residue. In line with this, a closer look at the release of CO and CO_2 revealed the lower production of gases. *Figure 9* shows the normalised production of carbon dioxide together with the theoretical behaviour of the non-interacting system, and the DTG curve against the sample temperature. It is evident how the release of CO_2 is strongly reduced at 250-500°C compared to the prediction of the additive reconstruction. The same result was obtained considering the release of CO.

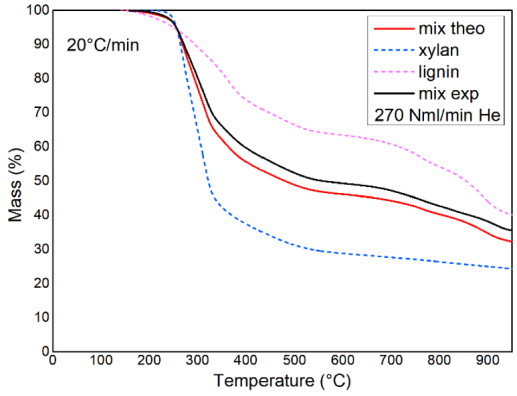

Figure 8: TG curves of xylan-lignin mixture at 20°C/min heating rate

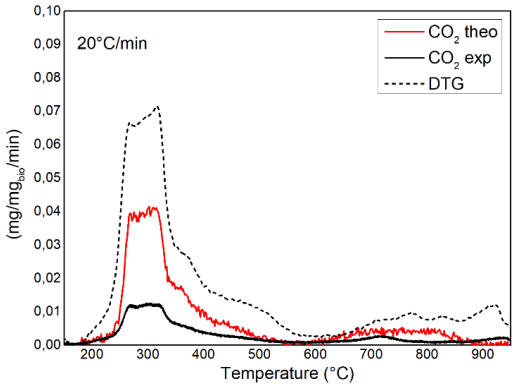

Figure 9: Xylan-lignin mixture, comparison of CO_2 production at 20°C/min heating rate

4. Conclusions

The growing interest towards potential sustainable fuels stems from the necessity of reducing energy-related CO_2 emissions. In this context, the valorisation of lignocellulosic biomass poses itself as a key step towards the independence of the energy sector from fossil fuels. This thesis focused on the pyrolysis of complex biomass feedstocks, whose understanding would represent a decisive achievement for the development of predictive lumped kinetic models and ultimately the optimization of bioenergy production processes.

The analysis on rice husk, a byproduct of rice milling, revealed a complex and multi-event devolatilization pathway, which is explained by the heterogenous chemical structure of the sample. A thorough study on the effect of the heating rate disclosed a shift in the onset temperature towards higher values as this parameter increased, while the solid residue remained unchanged. Moreover, the speciation of pyrolysis products unveiled a homogenous distribution between the categories of solid residue, bio-oil and gases. Another pivotal aspect of this work involved the assessment of an additive reconstruction of the sample making use of previously collected data on the pyrolysis of model biomasses (cellulose, hemicellulose, lignin) weighted on their mass fraction. From a general standpoint, the additive reconstruction (that is the simulation of the expected pyrolysis behaviour from non-interacting components) was able to predict the overall devolatilization and products' distribution of rice husk and no strong indications on the presence of synergistic effects have been found.

To better investigate the representativeness of studies based on physical mixtures of components, binary mixtures were tested and compared with the expected prediction for a non-interacting system. In the case of the cellulose-lignin mixture the prediction of the additive reconstruction systematically overestimated the production of volatile species and underestimated the yield of solid residue when compared to experimental results. Additional experiments performed with physically segregated components showed an improvement in the adherence to theoretical results, indicating that the physical contact at the particle scale between the components may paradoxically introduce effects of interactions. The nature of such effects has to be better investigated but it is believed that it could rely on the physico-chemical effect that the pyrolysis products from lignin (the component with lower devolatilization temperature) may exerts on cellulose. Regarding the xylan-lignin mixture, the general devolatilization trend was correctly captured by the additive reconstruction, although the yield of carbon monoxide and carbon dioxide was lower compared to the additive prediction.

In conclusion, this work shed light on significant insights on the pyrolysis of complex biomass feedstocks. Remarkably, the use of an additive modelling approach to predict the devolatilization and products' distribution of such samples provided better results for real biomass rather than the experiments from physical mixtures of model components.

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