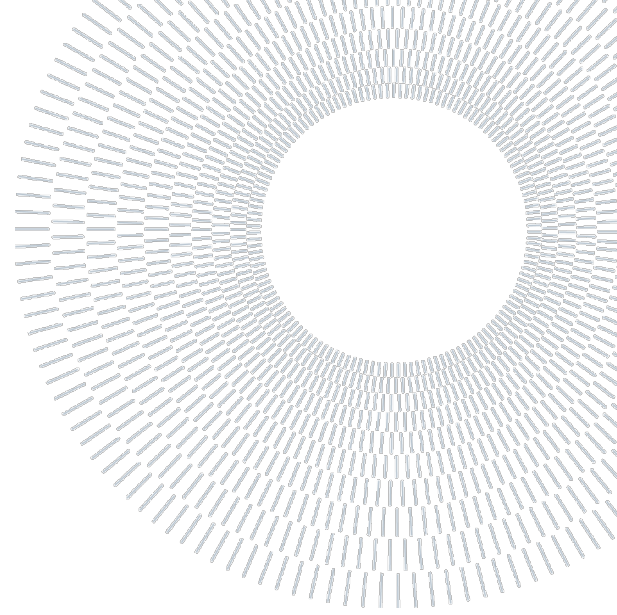




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EXECUTIVE SUMMARY OF THE THESIS

Experimental investigation on hemicellulose and biomass mixture pyrolysis: a study on devolatilization and speciation

TESI MAGISTRALE IN CHEMICAL ENGINEERING¹ AND ENERGY ENGINEERING² – INGEGNERIA CHIMICA¹ E INGEGNERIA ENERGETICA²

AUTHORS: ELEONORA BENEDETTO¹, ALESSANDRO RODA²

ADVISOR: ALESSANDRA BERETTA

CO-ADVISOR: VERONICA PIAZZA

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1. Introduction

In recent years, the escalating global demand for cleaner and sustainable energy sources has intensified the spotlight on biomass pyrolysis as a promising avenue for bioenergy production. Through the controlled application of heat in an oxygen-limited environment, biomass pyrolysis generates biochar, bio-oil, and syngas—versatile energy carriers that can be utilized for heat, power generation, and even as precursors for bio-based chemicals. [2] Lignocellulosic materials, derived from abundant and renewable resources, serve as one of the primary feedstocks for biomass pyrolysis and can be harnessed for the production of valuable products. [3,4] Within the spectrum of lignocellulosic biomass, hemicellulose emerges as a key component, acting as interfacial agent between cellulose and lignin. Hemicellulose is a branched polymer constituted of different monomers, mainly pentoses (d-xylose and l-arabinose) and hexoses (d-mannose, d-galactose, and d-glucose), whose specific composition varies among plant species. The

monomers are linked together through various types of glycosidic bonds, resulting in an amorphous structure with short chains and a low thermal stability compared to cellulose and lignin. These characteristics make hemicellulose a primary contributor to the bio-oil fraction during pyrolysis. [1,3,4] Understanding the pyrolytic behavior of hemicellulose becomes therefore imperative for optimizing bioenergy production processes. However, the literature currently lacks comprehensive information on the specific mechanisms and products resulting from hemicellulose pyrolysis, hindering the fundamental understanding of the process and impeding its optimization. The present study aims to investigate hemicellulose pyrolysis with a fundamental approach, unraveling key insights into its devolatilization behavior and elucidating its product yields and distribution. The first phase of the research, presented in paragraph 3.1, systematically examines the devolatilization of model molecules of hemicellulose using Thermogravimetric Analysis (TGA). The goal is to deepen the fundamental understanding of the process and gain reliable pieces of evidence to formulate accurate kinetic models and ultimately to

optimize process conditions. The second aspect of the investigation focuses on the speciation of pyrolysis products, as shown once again in paragraph 3.1. Various analytical techniques, including online Mass Spectrometry, offline Gas Chromatography, and Orbo™ sorbent traps, were employed for qualitative and quantitative analysis. The developed analytical protocol aimed to unravel the complex landscape of pyrolysis product yields and distribution resulting from hemicellulose degradation. Moreover, in recognition of the fact that in real biomass hemicellulose is typically interlinked with cellulose or other hemicelluloses, in paragraph 3.2 this study also delves into potential mixing effects. Mixtures of cellulose and hemicelluloses were prepared, and pyrolysis tests were performed to identify possible synergistic effects. Finally, data drawn from experiments carried out in a fixed bed reactor, a setup that enabled tests on a more representative scale, are discussed in paragraph 3.3 and compared to those obtained from the TGA-based campaign.

2. Materials and methods

The biomasses investigated in this experimental campaign were purchased from commercial sources: microcrystalline Cellulose powder was purchased from Sigma-Aldrich; beechwood Xylan powder, wheat Arabinoxylan powder and konjac Glucomannan powder were purchased from Megazyme and used as representatives of hemicellulose. To perform the pyrolysis investigations described in this work, a specialized experimental configuration is employed, depicted in Figure 1.

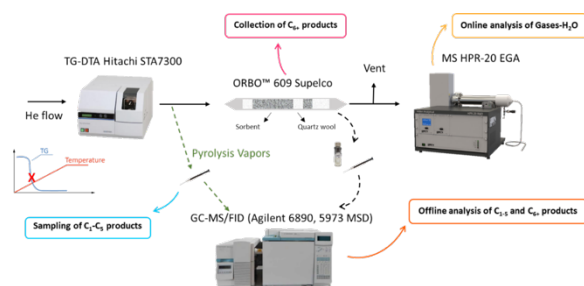


Figure 1: TGA-based setup for biomass pyrolysis tests with complete product speciation

A thermogravimetric (TG) analyzer, model Hitachi STA7300 TG-DTA, is employed for the execution of pyrolysis experiments. The process was divided in three phases: 40-minute at ambient temperature with a helium (He) flow to clear the system and eliminate oxygen, a gradual temperature increase

up to 950°C, maintaining He flow, in which pyrolysis takes place, and final 10-minute at 950°C with an air flow to burn condensed products and remove char residues. Each biomass sample underwent testing at three rates: 100°C/min, 20°C/min, and 3°C/min. The primary results of this analysis are the TG curves, where mass loss is plotted against temperature, and the DTG curves, employed to examine the sample's thermal behavior by illustrating the rate of change of mass as a function of temperature.

An in-depth investigation was also undertaken to quantitatively analyze pyrolysis products. To achieve this goal, a mass spectrometer (MS), model HPR-20 EGA from HIDEN Analytical, connected to the thermogravimetric analyzer (TGA) quantified gaseous products, while an offline gas chromatograph (GC), model Agilent 6890 Gas Chromatograph, was employed to quantify light compounds and heavy oxygenates. Gas analysis and heavy product trapping are performed within the same experiment, whereas light products sampling requires a separate run. In the first case the outlet of the TGA is connected to two Orbo™ 609 tubes on Amberlite® XAD®-2 (20/50) placed in series, subsequently linked to the inlet of the mass spectrometer. During pyrolysis, while heavy products are retained in the sorbent tubes, gases proceed undisturbed to enter the mass spectrometer for analysis. Here the software is configured to analyze specific ions corresponding to methane, water, carbon monoxide, methanol, and carbon dioxide. The Orbo™ trap is instead disconnected from the TG analyzer and its content is transferred into a vial and washed with a 10 mL solution comprising acetone and fluoronaphthalene (used as an internal standard for subsequent GC analysis). The eluted pyrolysis products are sampled and injected into the gas chromatograph. For speciation of light oxygenates, on the other hand, pyrolysis vapors are withdrawn directly from a sampling point located in the TG outlet line, and promptly injected into the GC for analysis. The analytical method in GC was optimized to separate the peaks relative to both light and heavy oxygenates. The products examined through gas chromatography include ketones, acids, C₅ and C₆ sugars, alcohols, furan derivatives, and cyclo-oxygenates. Two distinct outputs are used for analysis: the chromatogram and mass spectrum from the GC-MS and the chromatogram obtained through the GC-FID. The first one

is used for species identification, being each peak associated to a specific compound, while the second one is used for quantification, being the relative presence of each compound proportional to the integral area of its associated peak.

In order to achieve precise quantitative results a meticulous calibration of all instruments was conducted prior to the experimental campaign.

3. Results and discussion

The aim of the experimental campaign is to gain deeper insights on hemicellulose pyrolysis. Devolatilization trends were examined and the influence of key process parameters, such as heating rate, sample weight and carrier flowrate was investigated. The speciation of pyrolysis products instead aimed at identifying the species present in both gas and condensed phases and evaluate the yields of the main product categories—gases, bio-oil, and char.

3.1. Hemicellulose pyrolysis

As previously mentioned, devolatilization experiments are executed using a thermogravimetric analyzer (TGA). First, rigorous tests were undertaken to rule out the influence of the flow rate of the carrier gas and mass of the loaded sample. These experiments demonstrated that neither parameter affects the devolatilization of cellulose, xylan and glucomannan, while arabinoxylan is influenced on the solid residue. Still, this approach ensures that TG curves depend solely on the heating rate, enhancing the value of the obtained results for the development of kinetic models. Figure 2 illustrates Thermogravimetric and Derivative Thermogravimetric curves for xylan, glucomannan, arabinoxylan and cellulose. Overall, mass loss occurs within the same temperature range, between 200–400°C. However, the devolatilization profiles reveal distinct characteristics among polysaccharides. In particular, TG curves reveal that the pyrolysis of hemicelluloses has a lower onset temperature and yield a higher quantity of solid residue compared to cellulose.

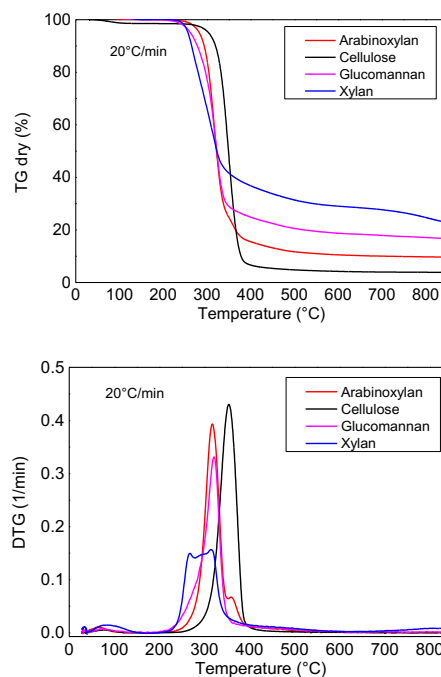


Figure 2: TG and DTG curves xylan, glucomannan, cellulose and arabinoxylan at 20°C/min and 229 ml/min of He

The DTG curves, where each peak represents a specific event, depict instead the multi-step nature of hemicellulose devolatilization: while cellulose exhibits a single, well-defined peak, glucomannan, features a unique peak with a secondary contribution, and arabinoxylan and xylan display two distinct peaks each. The complex profiles observed for hemicellulose devolatilization can be primarily attributed to their structural diversity. The amorphous structure facilitates the onset of devolatilization reactions, while branched chains consisting of various monomers and lateral substituents complicate the decomposition pathway, due to the multitude of bonds that must be broken.

Moreover, experiments were conducted under three distinct heating rates (3°C/min, 20°C/min, and 100°C/min) to examine the impact of this important parameter. A consistent trend emerged across all studied biomasses: with increasing heating rates, the onset temperature for devolatilization shifted to higher values while solid residue decreased, as shown in Figure 3. This phenomenon is expected and predominantly attributed to the dynamic nature of the TG experiment, where the duration varies significantly with the heating rate.

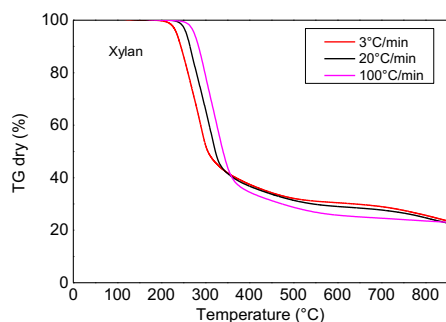


Figure 3: TG curves for xylan at varying heating rate and 229 ml/min of He

Fundamental in comprehending the pyrolysis process of hemicellulose is to achieve a thorough product speciation. Figure 4 shows the mass yields for pyrolysis products of xylan and glucomannan, categorized in char, bio-oil (comprising an organic phase and water), and gases. It is noteworthy that, despite the complexity of the analyzed systems, impressive balance closures have been achieved, registering respectively at 93.7% and 94.7%. The small discrepancy could be attributed to technical challenges encountered during the experiments, such as condensation of products or leakages in the lines, and to analytical issues.

Xylan exhibits higher water and gases mass yields (respectively 26.2% and 30.5% vs 16.1% and 12.6% for glucomannan), while glucomannan proves richer in bio-oil, particularly in the organic phase (45.9% vs. 12.9% for xylan) where anhydrosugars and furan derivatives, particularly C5 and C6 species, were prominent. In the case of xylan, other categories took precedence as well, with bio-oil organic products more homogeneously distributed but with lower mass yields.

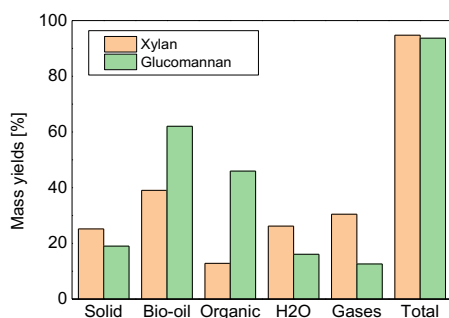


Figure 4: Xylan and glucomannan pyrolysis products

It is crucial to underscore that the achievement of a comprehensive balance has been realized through meticulous characterization of pyrolysis products

at the level of individual species, which, especially for the organic fraction of bio-oil, poses significant challenges. Identified species (40 for glucomannan and 29 for xylan) span a wide spectrum of classes, encompassing diverse functional groups and varying numbers of carbon atoms.

3.2. Biomass mixture pyrolysis

An additional pivotal aspect to be explored within the field of hemicellulose pyrolysis is the examination of mixtures. In natural sources in fact, hemicelluloses are never found as pure components but coexist with other constituents. Consequently, investigating the pyrolytic behavior of mixtures is important to elucidate possible interaction as well as synergistic effects between various components. Potential mixing effects have been investigated on both the devolatilization process and the subsequent product distribution of binary mixtures (50:50 wt%), which always included xylan, and of a quaternary mixture (25:25:25:25 wt%), comprising all studied biomasses. To achieve this, data pertaining to individual components were employed to compute the expected behavior for the mixture under the assumption of fully additive behavior, wherein each component contributes as an independent subsystem to the overall process. Therefore, TG and DTG curves and mass yields for pyrolysis products were derived for the theoretical mixture by averaging data for the individual components, according to their weight fraction in the real mixture. Subsequently, this theoretical projection was compared with experimental data.

In Figures 5, the TG and DTG curves for the xylan and glucomannan mixture are plotted. Data coming from the devolatilization of pure components, represented by dashed lines, and theoretical mixture data are also included. To ensure a comprehensive analysis, experiments were again conducted using three heating ramps (3°C/min, 20°C/min, and 100°C/min), mirroring the experimental conditions used for single biomasses. As a general trend experimental mixtures measurements matched those evaluated considering a fully additive behavior, as evidenced by an almost superimposable alignment of curves. This is particularly clear for low heating rates, when temperature control is improved and DTG curves are more definite. However, it is crucial to emphasize that the differences observed in the other cases are

minimal, and could be attributed to experimental errors, for example in the weighting phase.

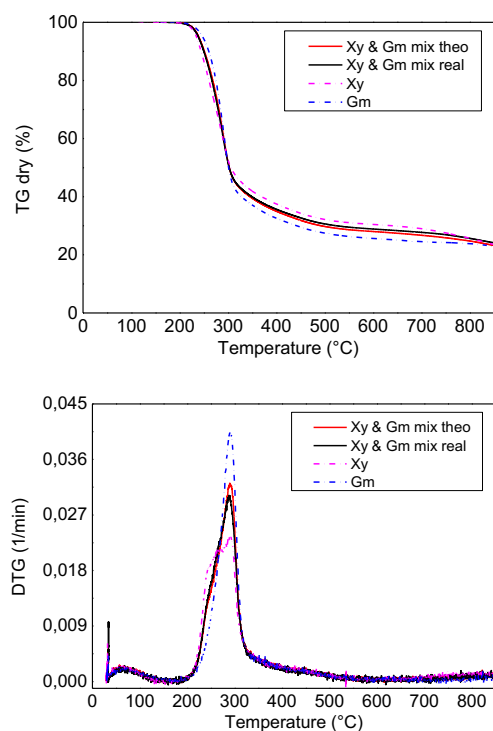


Figure 5: TG and DTG curves for xylan and glucomannan mixture with a heating rate of 3°C/min

All analyzed mixtures consistently adhere to the additive behavior, with minimal discrepancies often observed only in the initial stage of the reaction, where the real mixture shows a delay in the devolatilization. This behavior could be attributed to the glucuronic acid of xylan, which can be retained by the other component in the mixture, which has not undergone gasification yet.

For the speciation campaign a quantification was achieved in terms of gas, water and heavy oxygenates. In contrast, the speciation of light oxygenates was performed only on a qualitative basis. Quantification of light oxygenates proved to be challenging due to the nature of the analysis, which relies on a differential sampling of the Thermogravimetric Analyzer (TGA) effluent. This characteristic does not fit with the additive behavior of mixtures: each decomposition peak is related to the production of volatiles for each component present in the mixture and a single sampling point would not yield representative results for the whole mixture. In Figure 6 the quantification of products for the xylan and glucomannan mixture is illustrated. Mass yields for CO, CO₂, methane, methanol, water and levoglucosan are presented for the actual

mixture, the theoretical mixture and the individual components. As it is evident, the behavior of the real mixture generally aligns with the anticipated pattern, with very small differences between mass yields values.

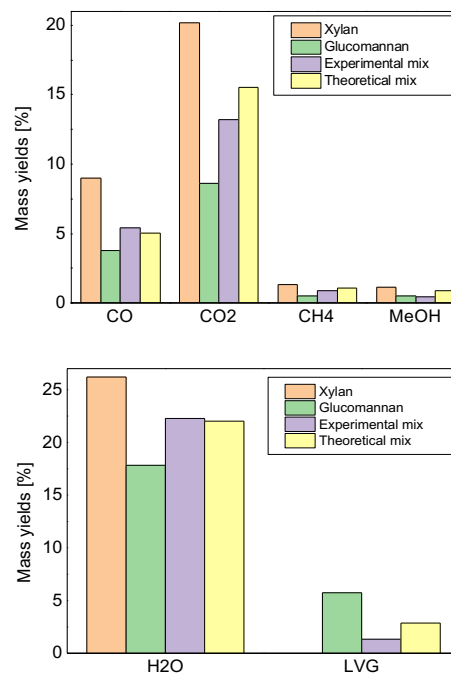


Figure 6: Xylan and glucomannan mixture product quantification

Despite not achieving satisfactory quantification results, a qualitative analysis for the bio-oil fraction remains feasible. Notably, all bio-oil components were identified in both the individual components and the mixture analysis, even if not quantified. In light of the considerations made thus far, it can be said that speciation experiments do not give strong evidence against additive behavior. However, it is also noticeable that a refinement in the experimental protocol is necessary to achieve a complete quantification and clearer indications towards additivity properties of mixture components.

3.3. Fixed bed reactor

An additional phase of this work involved the post-processing of data gathered from experiments which employed a fixed bed reactor, allowing tests on a more representative scale in terms of sample mass and flow rate. The main difference between TGA and fixed bed experiments consists in the temperature control: the former employs a heating rate which is controlled by the thermocouple of the

same weighing cell (in close contact with the sample), while the latter maintains an isothermal condition for the heating furnace. Given the fundamental influence of temperature on pyrolysis, variations are expected in the distribution of pyrolysis products, meaning that a comparison of the outcomes from the two setups could present challenges. Nevertheless, an integrated analysis remains highly valuable and has been conducted. As shown in Figure 7 cellulose exhibited the lowest yield of solid residue and the highest yield of bio-oil, xylan consistently displayed the largest solid residue, with products evenly distributed among all categories, and glucomannan demonstrated an intermediate behavior. These characteristics were consistently observed in both fixed bed and TGA experiments.

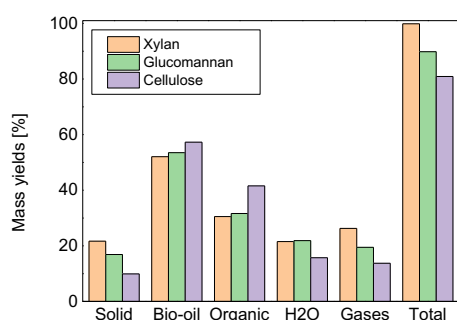


Figure 7: Xylan, glucomannan and cellulose pyrolysis products

Similar considerations can be made on mixtures. The additivity that was evidenced by TG and DTG curves, is also apparent in experiments conducted within the fixed bed configuration, as illustrated in Figure 8. Although some discrepancies may require further investigation, the general trend does not strongly indicate the presence of mixing effects and tends to confirm the initial hypothesis of additive behavior.

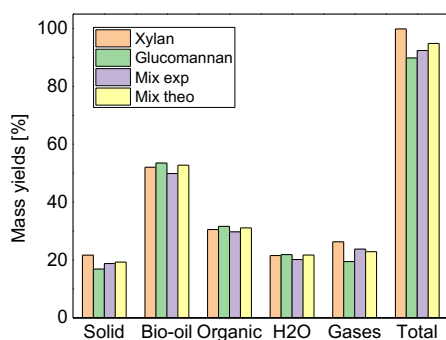


Figure 8: Xylan and glucomannan mixture pyrolysis products

4. Conclusions

In the pursuit of sustainable solutions to mitigate the escalating challenge of high CO₂ emissions in the energy sector, the utilization of lignocellulosic biomass as a renewable feedstock and its valorization through pyrolysis, emerge as a compelling strategy. This research has focused on the investigation of a less-explored class of biomass components—hemicellulose, addressing a noticeable literature gap by undertaking a comprehensive exploration into its pyrolysis, unraveling key insights into devolatilization behavior and product yields and distribution. Analysis on xylan, glucomannan, and arabinoxylan, revealed first of all a complex devolatilization pathway. TG and DTG curves showed changes in slope and multiple peaks, explained by the compositional diversity of hemicelluloses. A comprehensive study of the heating rate's impact unveiled then a consistent trend: increasing the heating rate led to a higher onset temperature of pyrolysis and a reduced solid residue. This is attributed to the dynamic nature of the TGA experiment, emphasizing the sensitivity of hemicellulose devolatilization to the rate of temperature increase. Categorization of the pyrolysis products demonstrated that bio-oil stood out as the primary pyrolysis product category, especially for glucomannan. Xylan on the other hand showed higher yields for water and gases. Despite the vast diversity of species individuated within the product slate an accurate quantification was achieved, with a remarkable balance closure. Another important outcome of this work involved investigating the pyrolysis of biomass mixtures. In this case, experimental results consistently supported the hypothesis of additive behavior: TG and DTG curves for real and theoretical mixtures closely matched, and product speciation gave no strong evidence of synergistic effects. For this latter campaign however issues regarding the analytical protocol for vapor sampling resulted in an incomplete quantification, making future adjustments necessary. Finally, data gathered from experiments conducted within a fixed bed reactor configuration, confirmed the results obtained so far, despite the inherent diversities between the two setups. In conclusion, this study underscores the critical significance of exploring the intricacies of hemicellulose pyrolysis, extending beyond the laboratory and offering tangible contributions to the ongoing global effort for a more environmentally conscious future.

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