

A COMBINED KINETIC AND EXPERIMENTAL APPROACH TO STUDY THE EFFECT OF THE ASH ON SLOW PYROLYSIS OF XYLAN

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ABSTRACT

This work focuses on the effect of ash during the slow pyrolysis of xylan. To this aim thermogravimetric and pyrolysis reactor tests, up to a temperature of 973 K at a heating rate of 5 K/min, were conducted for two samples: commercial (containing mainly Na and Ca ions) and demineralized xylan. Predictions were obtained with the Bio-PoliMI sub-mechanism of hemicellulose where the catalytic effect of ashes is included. In the case of predictions of the demineralized samples the effect of the ash was not included. Subsequently, the experimental and predicted mass loss profiles, product yields and gas composition were compared. The experimental results show that the commercial and demineralized xylan samples exhibit different pyrolytic behaviors that affect both the product yields and the gas phase composition. The kinetic mechanism is able to capture the mass loss profiles but fails to predict the gaseous species release profiles during the pyrolysis process. The predicted final yield of char is in agreement with the measurements, while the gas and bio-oil final yields are under and over predicted, respectively. Finally, the inclusion of the ash catalytic reaction had a marginal impact on the predictions.

Keywords: Xylan, Pyrolysis, Ash, Kinetic modeling

1. INTRODUCTION

One of the major concerns about the usage of biomass is the remarkable variety of its composition, in terms of both organic and inorganic matter, since it is known that small variations in their concentrations can affect the pyrolysis characteristic temperatures and product yields and compositions [1].

There are several studies that have focused on the effect of the ash in biomass pyrolysis and they all agree that the presence of these elements causes an increase in the yields of char and gas at the expense of pyrolysis liquids (i.e., dehydration, demethoxylation, decarboxylation), and charring reactions are enhanced, showing the catalytic effect inherent to the presence of the ashes. Therefore, the amount of low molecular weight and gaseous species increase and both primary and secondary reactions are affected, changing reaction paths and mechanisms [2]. However, these studies focused only on experimental studies. It is well known that the kinetic modeling of biomass pyrolysis is essential to define the progress of the decomposition-reaction paths and to evaluate the dependence of the rate of progression on process parameters. Nevertheless, most of the efforts were focused on the modification of the kinetic mechanism of cellulose pyrolysis [3] due to the lack of experimental data assessing the effect of metals on hemicellulose and lignin pyrolysis [4]. Very recently, Ranzi et al. [5] proposed a kinetic mechanism able to consider the catalytic effect of ashes not only during the pyrolysis of cellulose, but also of hemicellulose, where mass loss profiles, product yields formation and gas speciation are included. The authors observed that similarly to the case of cellulose, the presence of ashes in hemicellulose pyrolysis increase the formation of char and dehydration products while the formation of higher molecular weight species is inhibited.

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Hemicellulose constitutes about 20%-30% of the total mass of annual and perennial plants. It contains mainly D-xylose, D-mannose and D-galactose units. Xylan is often used as biomass hemicellulose representative in pyrolysis experiments due to its abundance in hardwood. However, the commercially available xylan is characterized by an extremely high content of ashes thus making the comprehension of its real decomposition mechanism quite challenging. To study the effect of ash on the slow pyrolysis of xylan, commercial and demineralized *beechwood* xylan were selected. These samples were subjected to pyrolysis tests up to a temperature of 973 K in both a thermogravimetric analyzer (TGA) and a pyrolysis reactor, under an inert atmosphere of nitrogen with a heating rate of 5 K/min. Weight loss profiles, product yields, and gas release rates as a function of the temperature were obtained. Finally, the experimental results were compared with the predicted values obtained using the hemicellulose sub-mechanism of the Bio-PoliMI, where the catalytic effect of the ash is included.

2. MATERIALS AND METHODS

2.1 Materials

Beechwood xylan (Sigma–Aldrich X4252) was used as hemicellulose representative. Raw xylan was demineralized as follows: 7 g of raw xylan were dissolved in 200 mL of distilled water and passed through 20 mL of cation-exchange resin (Dowex® 50WX8; H⁺ form). Then, the resulting eluate (pH around 2.5) was freeze-dried. No alterations both in the molecular weight and in the polysaccharide structure were detected by ¹H-NMR, FTIR and GPC (data not shown).

The total ash amount of raw (X) and demineralized xylan (DX) is 4.4 wt.% and 0.3 wt.%, respectively. The content of major inorganic elements was determined by Inductively Coupled Plasma Mass Spectrometry as reported in [2]. The X sample contains mainly, Na (21510 mg/Kg) and Ca (4909 mg/kg) ions. A significant removal of the metal ions in the DX sample is obtained through the demineralization process, being the final amounts of the Na and Ca ions 896 and 1031 mg/Mg, respectively.

2.2 Thermogravimetric and pyrolysis tests

The thermal behavior of the samples was studied in a thermogravimetric (TG) apparatus (Perkin-Elmer Pyris 1) by heating the sample (2-10 mg) from 323 K up to 973 K, at atmospheric pressure under an inert environment (N₂, 40 mL/min) using a heating rate of 5 K/min.

Pyrolysis tests in a pyrolysis reactor were performed at the same heating conditions as in the TGA. The residence time of the gas in the reaction chamber was 2 s, thus limiting the secondary reactions of the volatiles evolving from the primary decomposition of the xylan.

The pyrolysis reactor, described in detail elsewhere [6], consists of a steel jacketed prismatic chamber in which 6 g of sample are spread in thin layers (approximately 1 mm thick) over 4 sample trays, placed uniformly along the rectangular cross-section of the reaction chamber. The nitrogen flow is heated at the desired heating rate by a super heater and then enters the reactor jacket, reverses its flow and invests tangentially the sample. The temperature in the reaction chamber is monitored at the end of the sample trays by a N-type thermocouple. The gaseous stream that exits the reaction chamber passes through a condensation device. The non-condensing gases are fed to a micro gas chromatograph, equipped with a thermal conductivity detector (Agilent 3000 Quad) to obtain temporal profiles of the release rates of all the gaseous species evolving from the pyrolysis tests (CO, CO₂, H₂, CH₄, C₂H₄, C₂H₆ and N₂) [6].

2.4 Kinetic modeling

The kinetic modeling was performed using the Bio-PoliMI sub-mechanism of hemicellulose that considers the catalytic effect of ash [5] and the Cantera reaction kinetics library [7]. In the case of the DX sample, the ash catalytic reaction of the mechanism was not considered.

For the case of the hardwood samples, the Bio-PoliMI sub-mechanism of hemicellulose is described by four chemical reactions [5]. The inclusion of the catalytic effect of ash in the sub-mechanism of hemicellulose was performed as proposed by Ranzi et al. [5]. The kinetic parameters of the reaction of the hemicellulose intermediate (HCE1) were modified as a function of a non-dimensional global Ash Factor (AF).

3. RESULTS AND DISCUSSION

Figure 1 shows the experimental and predicted TG (a) and DTG (b) profiles of the xylan samples. Demineralized xylan decomposes over a short temperature range (473–573 K) with the main peak occurring at 523 K. A second small peak is detected between 560 and 660 K. Raw xylan decomposes over a wider temperature range, between 473 K and 623 K, and two distinct peaks can be detected at 510 K and at 550 K, respectively. The presence of metal ions in the X sample is responsible for the slight anticipation of the initial decomposition temperature and for the presence of a second peak at 550 K. The latter is only slightly visible at higher temperature in the DTG curve of DX. Moreover, in the case of the X sample, a higher amount of solid residue compared to the DX sample was obtained (29.7 wt.% for X and 25.5 wt.% for DX). The original kinetic mechanism slightly anticipates the experimental decomposition temperature of the DX sample in about 50 K. The weight loss curve shows two peaks at 508 and 585 K, thus not reproducing the main pyrolysis stage observed for the DX sample, whereas the yield of the final solid residue is slightly higher than the experimental value. The modified mechanism slightly anticipates the start of the pyrolysis process, but when compared with the results of the original mechanism, the impact is marginal. It predicts two decomposition steps, as the original mechanism, thus resembling the experimental behavior of the X sample. However, it is not able to reproduce with good accuracy the characteristic experimental temperatures of its decomposition. The experimental solid residue obtained for the X sample is predicted with good accuracy, but as for the DX sample, although the char yield slightly increases, the variation is marginal.

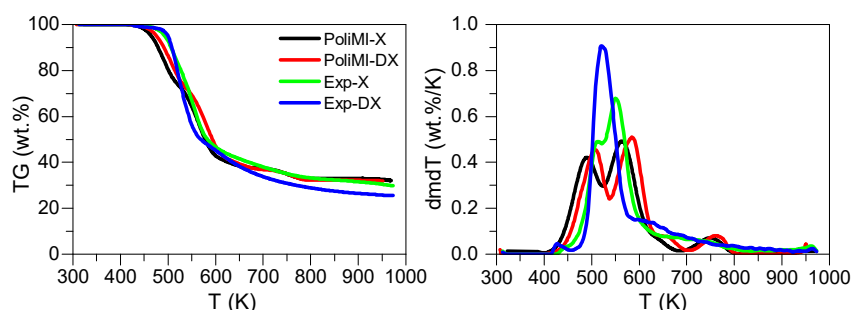


Figure 1. Experimental and predicted TG (a) and DTG (b) profiles of the xylan samples.

The char yields of the X and DX samples are very similar, even though, as for TG analysis, the char yield is slightly higher for the raw sample. The demineralization pre-treatment procedure results in a higher production of liquid products at the expense of gas. The original and modified kinetic mechanisms slightly over predicts the char yields of the DX and X samples, respectively, whereas the differences between numerical and experimental results are noticeable for bio-oil and gas yields. The mechanism, independently of the inclusion of ash, over predicts the gas yield at the expense of the bio-oil yield. Moreover, contrary to the experimental observations, the effect of the inclusion of ash on the predicted product yields is negligible.

Regarding the experimental and predicted cumulative volume and release rate profiles of the main gaseous species. The presence of ash in the X sample produces several effects: 1) it enhances the release of all the gaseous species in the whole temperature range; 2) it determines a high release of CO from the cleavage of the carbonyl groups in the low temperature region; 3) it shifts the release of H₂ as well as the maximum of the release rate curve toward lower temperatures, into the medium temperature region.

The original kinetic mechanism is not able to reproduce the experimental observations. Indeed, in the low temperature region two peaks of the same magnitude in the CO₂ and CO release rate curves are observed. CO₂ shows a third peak in the medium temperature region, whereas CH₄, H₂ and C₂H₄ start to release at very high temperature. The predicted cumulative volume of CO, CO₂ and C₂H₄ is significantly higher than the experimental ones, while the opposite trend is observed for H₂ and CH₄. The modified mechanism only determines an increase of the release of CO and CO₂ but to a lower extent with respect to the experimental observation. The differences in the predicted and experimental final cumulative volume of these two species are reduced with respect to the ash free case.

4. CONCLUSIONS

The experimental results show that 1) the initial decomposition temperature of the raw xylan is slightly anticipated with respect to the demineralized xylan, 2) there is a presence of a second important event in the pyrolysis curve of the raw xylan only slightly visible at higher temperature in the DTG curve of the demineralized xylan, and 3) the enhancement of the cracking reactions producing permanent gases (CO and CO₂) at the expense of pyrolysis liquids.

The kinetic mechanism is able to capture the mass loss profiles but fails to predict the gaseous species release profiles during the pyrolysis process. The predicted final yield of char is in agreement with the measurements, while the gas and bio-oil final yields are under and over predicted, respectively. Finally, the inclusion of the ash catalytic reaction had a marginal impact on the predictions.

Future work aims to face this mismatch between the experimental results and kinetic predictions. A modification of the model will be pursued applying the same approach used in Ferreiro et al. [6] based on the acquisition of experimental data on demineralized xylan doped with different concentrations of potassium and/or sodium chloride.

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