



Insights on the acetic acid pretreatment of wheat straw: Changes induced in the biomass properties and benefits for the bio-oil production by pyrolysis

Maurizio Pagano^{a,b}, Héctor Hernando^a, Jennifer Cueto^a, Pedro L. Cruz^c, Javier Dufour^{b,c},
Inés Moreno^{a,b}, David P. Serrano^{a,b,*}

^a Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, 28935, Móstoles, Madrid, Spain

^b Chemical and Environmental Engineering Group, Rey Juan Carlos University, c/ Tulipán, s/n, 28933, Móstoles, Madrid, Spain

^c Systems Analysis Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, 28935, Móstoles, Madrid, Spain

ARTICLE INFO

Keywords:

Wheat straw
Acetic acid washing
Pyrolysis
Bio-oil
Levoglucosan

ABSTRACT

This work discloses how the pretreatment of wheat straw with acetic acid (AA) solutions modifies the biomass composition, strongly affecting the pyrolysis product distribution. AA in diluted solutions is a renewable and eco-friendly reagent, being also one of the main components of the pyrolysis bio-oil* (water-free basis). In comparison with water and diluted ammonia treatments, AA washing leads to a higher removal degree of alkali and alkaline-earth elements (AAEMs) from the biomass ash. In addition, the AA pretreatment reduces the content of char and gas precursors, as is the case of soluble lignin and extractives. Consequently, the bio-oil* yield is drastically increased up to ~53 wt% during the pyrolysis of the AA washed wheat straw, being much higher than the value obtained for the raw biomass (~35 wt%). Likewise, the bio-oil* composition is highly improved by the pretreatment with AA, dramatically increasing the concentration and yield of levoglucosan, which is a valuable precursor to produce both advanced biofuels and bio-based chemicals. In contrast, the opposite occurs during the pyrolysis of the extracted matter samples, recovered from the washing solutions, since its high content of AAEMs, lignin and extractives promotes the formation of char and gases in the detriment of the bio-oil fraction. Based on a preliminary techno-economic analysis, it is concluded that pretreatment with AA solutions may improve significantly the economic performance of the wheat straw pyrolysis process. This is due to the increased incomes coming from the higher yield of both bio-oil* and levoglucosan that largely compensate the additional capital and fresh AA costs.

1. Introduction

Lignocellulosic biomass is a promising substitute for fossil fuels due to its wide availability and distribution, low cost, and near-zero net CO₂ emissions [1,2]. It is estimated that more than 180 billion tons of lignocellulosic biomass residues are generated every year from agricultural and forestry industries [3]. Thus, their use as an energy and chemical resource could help mitigate the problems associated with the management and disposal of these solid wastes which are usually burned in uncontrolled or low-efficient ways, contributing to the release of significant amounts of GHG into the atmosphere [4,5].

Lignocellulose is mainly constituted of three structural biopolymers: cellulose (40 – 60 wt%), hemicellulose (20 – 40 wt%), and lignin (15 – 25 wt%), whose proportion depends on the type of plant and their origin. In addition, it may also contain a variable proportion of non-

structural components such as acetyls, organic extractives (lipids, essential oils, proteins, simple sugars, etc.) and inorganic compounds, usually known as ash [6]. Typically, this mineral fraction contains significant amounts of alkali and alkaline earth metallic species (AAEMs), including potassium, calcium, and magnesium. The ash content is generally less than 1 wt% in woody biomass but it may represent up to 15 wt% in some herbaceous and agricultural residues [7,8].

The major challenge for lignocellulosic biomass valorization is the development of technically and economically feasible conversion routes. In this scenario, pyrolysis appears as an attractive option for biomass valorization due to its simplicity, low cost, and short operation times [9,10]. This process involves the thermal decomposition of biomass in the absence of oxygen at moderate temperatures (400 – 700 °C) under atmospheric pressure. During pyrolysis, the thermal conversion and depolymerization of cellulose, hemicellulose, and lignin

* Corresponding author at: Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, 28935, Móstoles, Madrid, Spain.

E-mail address: david.serrano@imdea.org (D.P. Serrano).

<https://doi.org/10.1016/j.cej.2022.140206>

Available online 7 November 2022

1385-8947/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

lead to the generation of three products: a carbonaceous solid, known as char, a pyrolysis gas, mainly composed of non-condensable gases such as CO, CO₂, H₂, and light hydrocarbons, and a liquid phase (bio-oil), which is considered as a potential precursor for the production of biofuels and/or high-value-added bio-based chemicals [11,12]. However, the final use of the bio-oil is limited to low-quality applications due to its high contents of water and oxygenated compounds (acids, furans, sugars, aldehydes, phenolics, ethers, esters, lignin oligomers, etc.), which results in a high instability and viscosity, extremely acidic pH and low heating value [13].

The yield and properties of the pyrolysis bio-oil strongly depend on the chemical composition and structure of the biomass used as feedstock as well as on the operating conditions of the pyrolysis process. In this sense, one of the biomass components that most significantly influence the pyrolysis process, despite their low concentration, are alkali and alkaline earth metals (AAEMs). These elements are typically present in the form of water-soluble salts (mainly Na and K) as well as under mineral and/or organically-bonded states (i.e. Ca and Mg) [14]. AAEMs promote char forming and fragmentation reactions, reducing the bio-oil yield [15–17]. In particular, monovalent Na and K catalyze anhydrosugars dehydration. In addition, K favors the formation of polyphenols, at the expense of monophenols, and enhances the generation of light molecules such as acids and short aldehydes, which accelerate the bio-oil aging and reduce the selectivity towards added-value chemicals [16–18].

Water has been employed for lignocellulose deashing, although being only effective for the elimination of water-soluble AAEMs species [14,19]. In contrast, biomass washing with inorganic acids (typically HNO₃, H₂SO₄, HF, HCl, etc.) has been reported to lead to a high degree of demineralization [7,20–23]. However, washing pretreatment with these strong mineral acids may alter significantly the physicochemical structure of the biomass [7,23], while it cannot be considered a green process due to the generation of high volumes of polluted aqueous streams. Interestingly, the use of organic acids for biomass deashing to improve bio-oil production during the pyrolysis process has been quite less investigated. In particular, lignocellulose washing with acetic acid can be highly interesting as it is one of the main components typically detected in bio-oils, which would lead to a self-sustained and eco-friendly process. In this sense, acetic acid should be recovered from the bio-oil to be used as a washing agent. For that purpose, different strategies have been recently explored such as fractional condensation [24,25], reactive distillation combined with esterification [26], extraction using organic solvents [27], membrane filtration technologies [28] or anion-exchange columns [29].

Although the extraction of acetic acid from the pyrolysis bio-oil is still under study, there is enormous potential for its use as a washing agent for the demineralization of biomass, especially those with high ash contents, since it can be considered an eco-friendly reagent of renewable origin. In this context, biomass demineralization using acetic acid or even the bio-oil aqueous phase (which contains acetic acid and lights hydrophilic oxygenates) and their effect on the pyrolysis process have been explored in recent years [19,30,31]. However, these results are often based on TG/FT-IR analyses and, in most cases, non-direct indications about the lignocellulose structural modifications are provided. On the other hand, the improvement of the bio-oil quality is usually determined in terms of the area of GC–MS analyses, which is a semi-quantitative approach.

In this sense, the current work investigates the effect of using acetic acid as a bio-based green solvent for the pretreatment of a lignocellulosic biomass (wheat straw) on its composition and how this influences the product distribution when subjected to a pyrolysis process. Moreover, the pretreatment with acetic acid solutions of different concentrations is compared with washing using both diluted ammonia and hot water. The article discloses that the acetic acid washing provokes a great enhancement in the yield of the pyrolysis bio-oil fraction, improving also significantly its composition as denoted by the sharp increase

observed in the levoglucosan concentration, which is a highly valuable compound used as a precursor of both advanced biofuels and bio-based chemicals. The article deals also with the properties and pyrolysis behavior of the extracted matter, recovered from the washing solutions. This comprehensive study has allowed us to get a full understanding of the changes induced by the washing treatments on the biomass properties and how this benefits the bio-oil production during pyrolysis.

2. Materials and methods

2.1. Biomass washing pretreatment

For this study, wheat straw (WS) coming from Segovia (Spain) was selected as a representative residue of the agricultural industry. Previously to the washing pretreatments and characterization analyses, wheat straw was grounded in a cutting mill and sieved to a particle size of 0.5–1 mm. Then, several fractions of this biomass were washed with water, with a 2.5 wt% aqueous solution of NH₃ (J. T. Baker, 28–30 wt %), and with diluted acetic acid (AA) (Sigma-Aldrich, purity >99.5 wt %) in different concentrations (0, 0.25, 0.5, 0.75, 1, 2.5, 5, and 10 wt%). For that, WS was mixed with the washing solution using a mass ratio of 1:20 (and additionally 1:12 in the case of AA) at 50 °C for 2 h under continuous magnetic stirring. Thereafter, the mixture was filtered under vacuum and, in the case of AA and NH₃ washings, rinsed with deionized water until reaching a neutral pH [32]. The recovered solid samples were oven-dried at 90 °C for 48 h and then weighted to determine the mass loss produced during the washing pretreatments. The pretreated WS samples were labeled as follows: WS-X-Y, where X denotes the washing agent employed (H₂O, AA or NH₃) and Y indicates the AA or NH₃ concentration (2.5 wt% for NH₃ or 0.25, 0.5, 0.75, 1, 2.5, 5 and 10 wt% for AA). Washing yields were calculated according to Eq. (1):

$$W_{WS-X-Y}(\text{wt}\%) = 100 \cdot \left[\frac{\text{dry washed biomass (g)}}{\text{dry raw biomass (g)}} \right] \quad (1)$$

Three samples of filtrated solutions (those corresponding to the washings with water, 2.5 wt% of acetic acid and 2.5 wt% of NH₃) were dried in a rotary evaporator to recover the organic and inorganic solid fractions (extracted matter, EM) leached during the washing treatment.

2.2. Biomass characterization

Proximate analyses of raw wheat straw and samples subjected to the washing pretreatments were performed following European the standards procedures UNE-EN ISO 18134-1:2016, UNE-EN ISO 18122:2016 and UNE-EN ISO 18123:2016 to determine the moisture, ash, and volatile matter contents, respectively. Accordingly, moisture percentage was estimated by the difference of weight after heating the sample in an oven at 105 °C overnight while the mineral fraction (ash) content was calculated by weighting the sample residue obtained by calcination in a muffle furnace at 550 °C for 1 h under static air conditions. Volatile matter content was determined by thermogravimetric analysis (TGA) under inert flow using a thermobalance NETZSCH STA 449, heating the sample up to 900 °C at 10 °C/min, followed by an isothermal step of 10 min. Finally, the fixed carbon percentage was calculated by the difference between those values and the initial sample weight. To determine the effect of washing treatments on biopolymers decomposition temperature, thermal gravimetric analyses (TGA) were performed using a NETZSCH 449 Thermobalance, under an inert atmosphere with a heating rate of 5 °C/min up to 900 °C. The chemical composition of the mineral fraction (ash) recovered from the calcination of raw wheat straw, as well as that of washed samples, were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Perkin-Elmer Optima 7300 DV instrument. Before these analyses, the samples were acid digested under microwave heating radiation. The difference with the total amount of ash sample is denoted as “others”. This fraction

is mainly composed of silica, whose concentration could not be determined reliably by ICP analyses, and minor traces of Ba, Cu, Ni, Ti, Zn. [32–34]. Elemental organic C, H, and N composition was determined using a Thermo-Scientific Flash 2000 microanalyzer, calculating O content by difference, after subtracting the ashes.

Determination of biopolymers content (cellulose, hemicellulose, lignin, and extractives) of raw WS and washed WS-H₂O, WS-NH₃-2.5, and WS-AA-2.5 samples were performed using an adapted procedure from the National Renewable Energy Laboratory described in the literature [35]. Biopolymers composition of EM samples was calculated by difference according to Eq. (2):

$$EM-X_z(\text{wt.}\%) = 100 \cdot \frac{WS-Raw_z - WS-X_z \cdot W_{WS-X-Y}}{(1 - W_{WS-X-Y})} \quad (2)$$

where z = cellulose, hemicellulose, lignin, acetyls or extractives content (wt.%).

2.3. Pyrolysis tests

To investigate the effect of the washing pretreatment on the bio-oil yield and composition, a set of pyrolysis assays were performed using, as feedstock, the raw wheat straw, the samples washed with water (WS-H₂O) and aqueous solutions of 2.5 wt% of NH₃ (WS-NH₃-2.5) and 2.5 wt% of acetic acid (WS-AA-2.5) and the corresponding fractions of extracted matter (EM). An additional pyrolysis test was carried out by feeding the WS sample washed with 0.75 wt% of acetic acid solution and a water:biomass mass ratio of 12:1 (WS-AA-0.75). These experiments were carried out under an oxygen-free environment and atmospheric pressure using a downdraft stainless steel reactor (16 mm i.d. and 400 mm length) equipped with two independent heating zones (upper and lower zones), the temperatures of which were set at 550 °C and 450 °C, respectively. A full description of the reaction setup and sample collection system was detailed in previous works [33,36–38]. Typically, 4 g of the feed sample were loaded in the feedstock tank. The reaction system was subsequently purged using 100 ml/min of N₂. Once both reaction temperatures were reached, the biomass was discharged into the reactor, being thermally decomposed to yield a solid residue (char) and a volatile fraction, which left the reactor through a condensation trap cooled by an ice-water bath, where the pyrolysis bio-oil was collected. The volume of non-condensable gases produced was quantified using a drum-type gas meter (Ritter TG0.5/5) while the volumetric concentration of H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₈ and C₄H₁₀ were analyzed in a Micro-GC Agilent 490 equipped with molecular sieve (Molsieve 5 Å) and PPQ columns and a thermal conductivity detector (TCD).

Both proximate and elemental analyses of the char fraction were performed according to the same European Standard procedures used for the initial biomass characterization. Bio-oil water content was estimated by Karl-Fischer titration (Mettler-Toledo, V20). This value allowed the organic percentage present in the liquid fraction to be determined (i.e. bio-oil on a water-free basis), which was denoted as *bio-oil**. Bio-oil chemical composition was analyzed by gas chromatography-mass spectrometry (GC-MS) in an Agilent 8860 GC-5977B GC/MSD instrument equipped with a fused silica HP5-MS UI column (30 m × 0.25 mm × 0.25 mm). NIST 2017 spectral library was employed for the identification of compounds having a minimum matching factor of 85/100 (typically over 90/100). Before the analyses, the bio-oil samples were diluted in dioxane (1:10 mass ratio) and 1000 ppm of cyclohexanol was added as an internal standard. The main components in each family (acids; ketones, esters, and ethers; aliphatic compounds; aromatics; furans; oxygenated aromatics, and sugars) were calibrated to estimate their mass concentrations from the respective response factor using the internal standard calibration method. A mean response factor, determined from those of the calibrated molecules of each family, was applied to determine the concentration of the non-calibrated molecules

present in lower amounts (typically <1 % relative GC/MS peak area). The percentage of bio-oil* quantified by GC-MS was estimated as the sum of the mass concentrations of all compounds detected by GC-MS analyses regarding the total amount of bio-oil*. This parameter was denoted as *bio-oil* total detected fraction*.

The reaction mass balance was calculated from the weight of the products collected at the end of the experiments and, in all cases, closed with an experimental error of less than 5 % compared to the amount of initial biomass loaded into the reactor. Then, product yields were determined according to Eq. (3):

$$\text{Mass yield}_i(\text{wt.}\%) = 100 \cdot \left[\frac{\text{mass}_i(\text{g})}{\text{biomass}(\text{g})} \right] \quad (3)$$

where i = gas, char, bio-oil* and water. Results from pyrolysis of washed WS and EM samples were combined with the respective washing yields to calculate a weighted sum for reaction yields, gas and bio-oil* composition, according to Eq. (4):

$$(WS + EM)_y \text{ yield}_i(\text{wt.}\%) = WS_y \text{ yield}_i \cdot W_{WS-X-Y} + EM_y \text{ yield}_i \cdot (100 - W_{WS-X-Y}) \quad (4)$$

where y denoted the washing pretreatment (H₂O, 2.5 % AA or NH₃ washed samples) while i designated the pyrolysis product (i.e. gas, bio-oil*, H₂O, char, CO, CO₂, sugars, acids, etc.).

3. Results and discussion

3.1. Effect of the washing pretreatments on the biomass properties

In this study, three types of washing solutions (water, diluted acetic acid or NH₃) were used in the pretreatment of wheat straw. In the case of acetic acid, the biomass washing was performed varying its concentration in the range of 1 – 10 wt%.

First, the influence of the washing pretreatments on the chemical and structural properties of the raw biomass was evaluated (Table 1). Pure water leads to the highest washing yield (88.9 wt%), although this value indicates that the proportion of extracted matter is not negligible. The use of a weak acid (AA) slightly decreases the biomass yield (about 88 wt%) in comparison with water, whereas almost no variations in this parameter were observed when varying the AA concentration. In contrast, the utilization of diluted NH₃ as a washing reagent extracts a higher proportion of matter, showing washing yields of 84.7 wt%.

Proximate and ultimate analyses of raw biomass and washed samples are also shown in Table 1. All pretreatments decrease the ash content of the initial biomass. Water washing leads to a limited ash removal of the raw biomass with a demineralization degree of just 9 wt%. The reduction in the mineral matter content increases when acetic acid is the washing reagent, achieving values in the range of 16.0 – 18.7 wt%, with no significant differences with the AA concentration. The highest demineralization percentage is attained by using diluted ammonia, which eliminates more than 40 wt% of the inorganic matter present in the raw wheat straw. Interestingly, the washing pretreatments also modify the composition of the biomass as reflected in the changes produced in both proximate and elemental analyses. In general, a decrease in the fixed carbon content is observed in all cases, resulting in an increase in the volatile matter share. Thus, after water washing the fixed carbon passes from 21.3 wt% to 15.0 wt%, whereas the volatile matter content is augmented from 71.8 wt% to 79.2 wt%. These results evidence that just washing with hot water (50 °C) provokes significant changes in the distribution of the organic components present in the raw wheat straw. However, the elemental composition of biomass in terms of C, H, N, and O content is little affected by the pretreatments. In this way, the major variations are appreciated in the case of washing with diluted AA solutions, leading to an increase in the carbon content and a reduction in that of the oxygen.

Table 1
Proximate and ultimate analyses of raw and washed WS samples (wt%).

| Sample | WS-Raw | WS-H ₂ O | WS-NH ₃ -2.5 | WS-AA-1 | WS-AA-2.5 | WS-AA-5 | WS-AA-10 | Error (±wt.%) |
|--------------------|--------|---------------------|-------------------------|---------|-----------|---------|----------|---------------|
| Washing yield | – | 88.9 | 84.7 | 87.3 | 88.1 | 87.7 | 88.4 | 0.6 |
| Moisture | 3.6 | 2.8 | 4.6 | 1.8 | 2.0 | 1.9 | 2.2 | 0.01 |
| Volatile matter | 71.8 | 79.2 | 77.3 | 78.6 | 79.6 | 78.3 | 78.5 | 0.5 |
| Fixed carbon | 21.3 | 15.0 | 16.2 | 16.9 | 15.7 | 17.0 | 16.6 | 0.5 |
| Ash | 3.3 | 3.0 | 2.0 | 2.8 | 2.8 | 2.8 | 2.7 | 0.3 |
| % Demineralization | – | 9.0 | 41.0 | 16.0 | 16.9 | 16.3 | 18.7 | 1.00 |
| C | 44.9 | 45.3 | 46.0 | 47.1 | 47.1 | 46.3 | 46.8 | 0.3 |
| H | 5.8 | 5.9 | 6.1 | 6.0 | 6.0 | 5.9 | 6.0 | 0.05 |
| N | 0.5 | 0.3 | 0.3 | 0.7 | 0.4 | 0.3 | 0.3 | 0.04 |
| O | 45.5 | 45.6 | 45.7 | 43.4 | 43.7 | 44.7 | 44.3 | 0.4 |

As typical herbaceous biomass, wheat straw ash is rich in SiO₂ and alkali and alkaline earth metals (AAEMs) [32]. AAEMs are known to catalyze secondary cracking reactions that reduce bio-oil* production and increase gas and char yields [32,39,40]. Ash composition determined from ICP-OES analyses is depicted in Fig. 1. As it can be appreciated, K (4548 ppm) and Ca (1159 ppm) are the most abundant AAEMs in the ash of the raw wheat straw, followed by smaller proportions of Na (501 ppm) and Mg (418 ppm). K is the metal with the highest catalytic activity interfering in the biomass pyrolysis process among the AAEMs according to the literature [15,41]. Its content decreases by 68.3 % and 87.2 % when treating the WS with H₂O and NH₃, respectively, while low concentrations of AA are sufficient to almost completely eliminate this element, reaching a decrease of ca. 99 %. Similarly, Na content is only partially removed with water and ammonia washings, but it is strongly reduced (by ca. 98 %) when using low concentrations of AA. Water treatment does not eliminate Ca and Mg, whereas ammonia washing is partially effective. In the case of AA, the leaching of Ca and Mg takes place in a higher extension, mainly when increasing the concentration of this acid reagent. In summary, low concentrations of acetic acid are sufficient to eliminate almost all AAEMs, while water treatment is less effective. Ammonia's capacity of eliminating AAEMs is in between the previous pretreatments, despite this basic reagent caused the highest reduction in the overall ash content. This fact can be related to the significant reduction in the "others" group produced by ammonia washing as it dissolves preferentially the silica, which is the main constituent of the mineral fraction of raw wheat straw. SiO₂ is considered an inert material without significant catalytic effects in biomass pyrolysis processes.

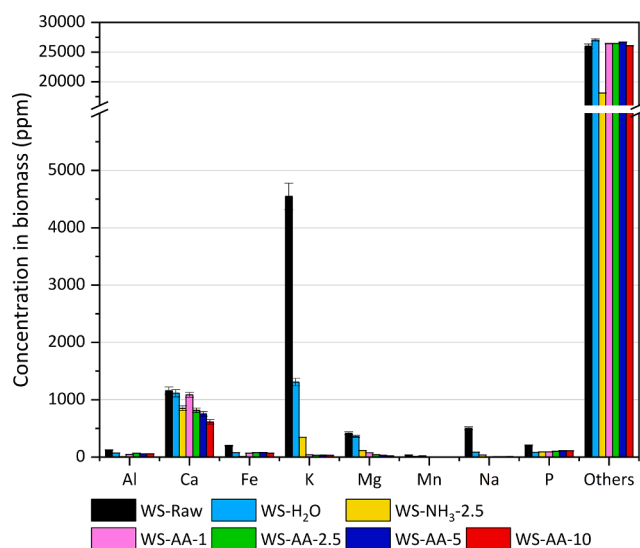


Fig. 1. Ash composition of raw and washed WS samples determined by ICP-OES analyses.

Thermogravimetric analyses were performed to investigate the effect of pretreatments on biopolymers degradation temperature (cellulose, hemicellulose, and lignin). The weight loss and DTG curves are shown in Fig. 2. For the sample WS-Raw the main weight losses are observed in the temperature range of 160 – 400 °C, a shoulder at 282 °C followed by a major peak centered at 319 °C being appreciated in the DTG profiles, which is attributed to the overlapped breakdown of hemicellulose and cellulose, respectively. Hemicellulose, consisting of branched polymers of five and six carbon sugars, degrades at lower temperatures (250 – 340 °C) than cellulose, which is a linear polymer of glucose (340 – 400 °C). Lignin decomposes in a quite broad temperature interval (200 – 700 °C), hence its weight loss is not clearly defined, partially overlapping with those of cellulose and hemicellulose. Water, ammonia and the different acetic acid treatments give similar results: they reduce the overlapping between the polysaccharides by shifting cellulose conversion to higher temperatures, passing from about 319 °C for WS-Raw to ca. 344 °C in the case of WS-NH₃-2.5. Other noticeable effect is that the shoulder present in the raw WS at about 220 °C disappears after the washing pretreatments. Consequently, the hemicellulose peak becomes better defined, showing clearly a maximum in the range of 281 – 292 °C. On the other hand, the broad lignin degradation signal at about 400 °C is not significantly affected by any of the investigated pretreatments. Reducing the overlapping in the thermal decomposition of cellulose and hemicellulose could facilitate the development of fractional pyrolysis processes, allowing two or more bio-oil streams with a more uniform chemical composition to be produced [42].

The above results indicate that acetic acid pretreatments show the best performance in terms of AAEMs removal from the raw biomass, hence having a high potential to improve the biomass pyrolysis process. In addition, comparing with mineral acid pretreatments extensively investigated in the literature, it presents the advantages of being a non-toxic and renewable origin substance. Moreover, acetic acid is a product of biomass pyrolysis itself, being one of the main components typically detected in the bio-oil aqueous phase. As concluded from the previous results, acetic acid concentrations higher than 2.5 wt% do not provoke a noteworthy improvement in the demineralization efficiency. Accordingly, the washing solution with 2.5 wt% of AA was selected for the subsequent characterization and pyrolysis tests.

Although the biomass yield after the washing pretreatment is relatively high (between ca. 85 and 89 wt%), these figures denote that the amount of extracted components is clearly superior to the ash removal, and even significantly higher than the overall content of mineral matter in the raw WS. This fact, along with the changes observed in the proximate and ultimate analyses and the TG profiles, evidences that a significant part of the organic components is also extracted during the washing pretreatments. In order to get further insights into its nature, the extracted matter (EM) was recovered by evaporation and characterized (Table 2). Proximate analysis shows that all EM samples are richer in fixed carbon and ash, having lower volatiles and moisture contents than the starting biomass. These results suggest that the pretreatments selectively extract substances that are more susceptible to be

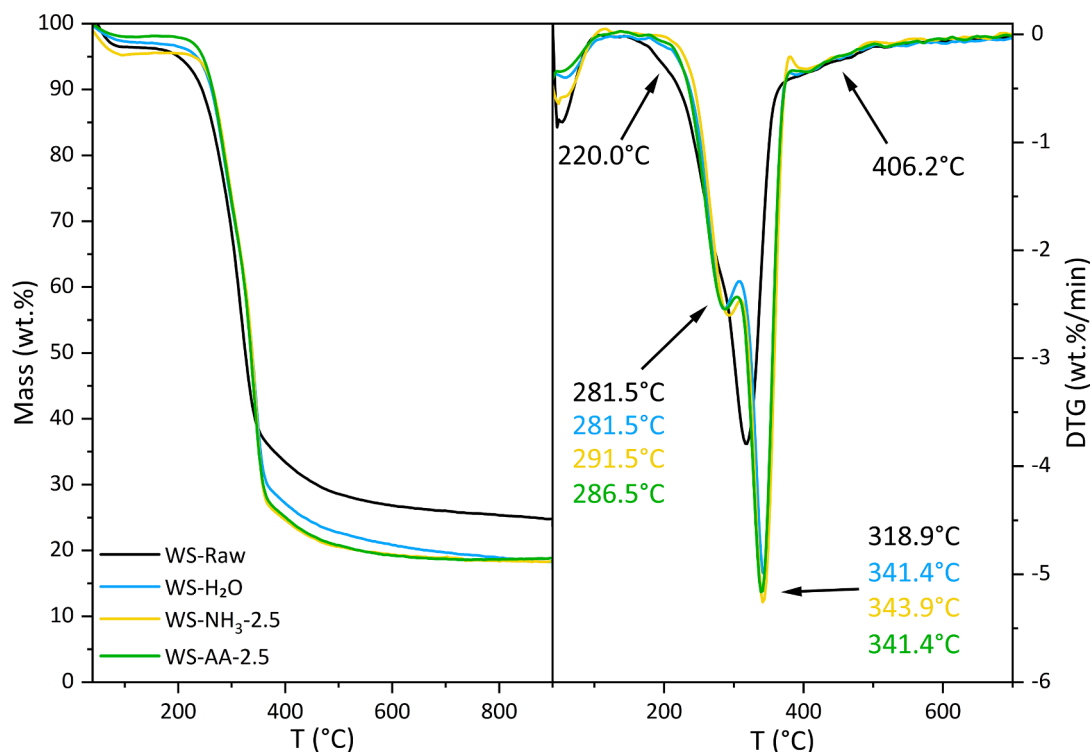


Fig. 2. TG/DTG profiles of untreated and washed WS samples.

Table 2
Proximate and elemental analyses of raw WS and EM samples (wt%).

| Sample | WS-Raw | EM-H ₂ O | EM-NH ₃ -2.5 | EM-AA-2.5 | Error (±wt. %) |
|-----------------|--------|---------------------|-------------------------|-----------|----------------|
| Yield | — | 11.1 | 15.4 | 11.9 | 0.5 |
| Moisture | 3.6 | 5.7 | 4.1 | 4.9 | 0.01 |
| Volatile matter | 71.8 | 62.2 | 59.7 | 64.1 | 0.4 |
| Fixed carbon | 21.3 | 26.4 | 25.4 | 23.5 | 0.5 |
| Ash | 3.3 | 5.8 | 10.8 | 7.5 | 0.4 |
| C | 44.9 | 42.0 | 42.8 | 41.8 | 0.2 |
| H | 5.8 | 5.6 | 5.6 | 5.1 | 0.04 |
| N | 0.5 | 1.6 | 1.1 | 1.7 | 0.1 |
| O | 45.5 | 45.0 | 39.4 | 43.6 | 0.2 |

converted into char in addition to the ash removal. Elemental analysis of EMs (Table 2) shows that they all have a slightly lower carbon content than washed samples. The oxygen content of EM is very similar to the respective washed sample in the case of water and acetic acid, while EM-NH₃-2.5 presents a lower value. However, the oxygen contents of the three EM samples are clearly superior to the values expected from lignin-like species (ca. 25 – 30 wt%), showing that the washing pretreatments also affect other components in the raw biomass, mainly complex molecules typically considered as extractives but different from the lignocellulose biopolymers. This conclusion agrees well with the absence of the low temperature (ca. 200 °C) signal in the DTG curves after the washing pretreatments.

Characterization analyses of the different biomass components have been performed over the two fractions (washed samples and extracted matter) obtained after washing with H₂O, 2.5 % NH₃ and 2.5 % AA (Fig. 3). Apart from the main structural polymers, the concentration of acetyls, acid-soluble lignin and extractives has been also determined. Acetyls groups are present on the side chains of lignin and hemicellulose, being one of the main acetic acid sources during pyrolysis [43], whereas acid-soluble lignin consists of the external syringyl groups that

are present in the lignin structure. This last component is quantified differently from lignin since the reactivity of the functional groups can interfere with the quantification of non-acid-soluble lignin [44]. On the other hand, extractives are a set of organic compounds that are not an integral part of biomass polymeric structure. They include saccharides and other carbohydrates, proteins, phenols, organic acids, resins, waxes and sterols among many other compounds [45], so an exhaustive characterization of these components is difficult to be performed. The raw WS is rich in cellulose (32.6 wt%) followed by hemicellulose (27.2 wt%), lignin (18.8 wt%) and extractives (10.8 wt%). The other components such as acetyls and acid-soluble lignin are present in smaller amounts.

In general, ash, acetyl groups, extractives and a small fraction of lignin are selectively leached to form EM with any solvent used. Ammonia is particularly effective in extracting acetyls, their concentration increasing from 11.5 wt% in EM-H₂O to 20.5 wt% in EM-NH₃-2.5, while no significant changes are observed with respect to water washing when using acetic acid. Water mainly solubilizes extractives since they represent 51.1 wt% of EM-H₂O, presenting a limited ability to attack and break leakages of biomass structural polymers under the pretreatment conditions here applied. Regarding the polysaccharide content, it can be seen that acetic acid extracts cellulose (15.0 wt% in EM-AA-2.5) while water and NH₃ only dissolved a small amount of hemicellulose (ca. 8 wt% in EM-H₂O and EM-NH₃-2.5). As a result, holocellulose concentration increases in all washed samples, while lignin extraction is not sufficient to significantly change its concentration in any case. As shown in Fig. S1, a great part of the weight loss during TG analysis of EM samples occurs at relatively low temperatures (170 – 270 °C), which agrees well with being formed mostly by non-polymeric species (extractives), while a minor weight loss can be appreciated at temperatures that correspond to lignin degradation (420 – 460 °C).

3.2. Effect of the washing pretreatments on the biomass pyrolysis products

After studying how the washing treatments affect WS composition,

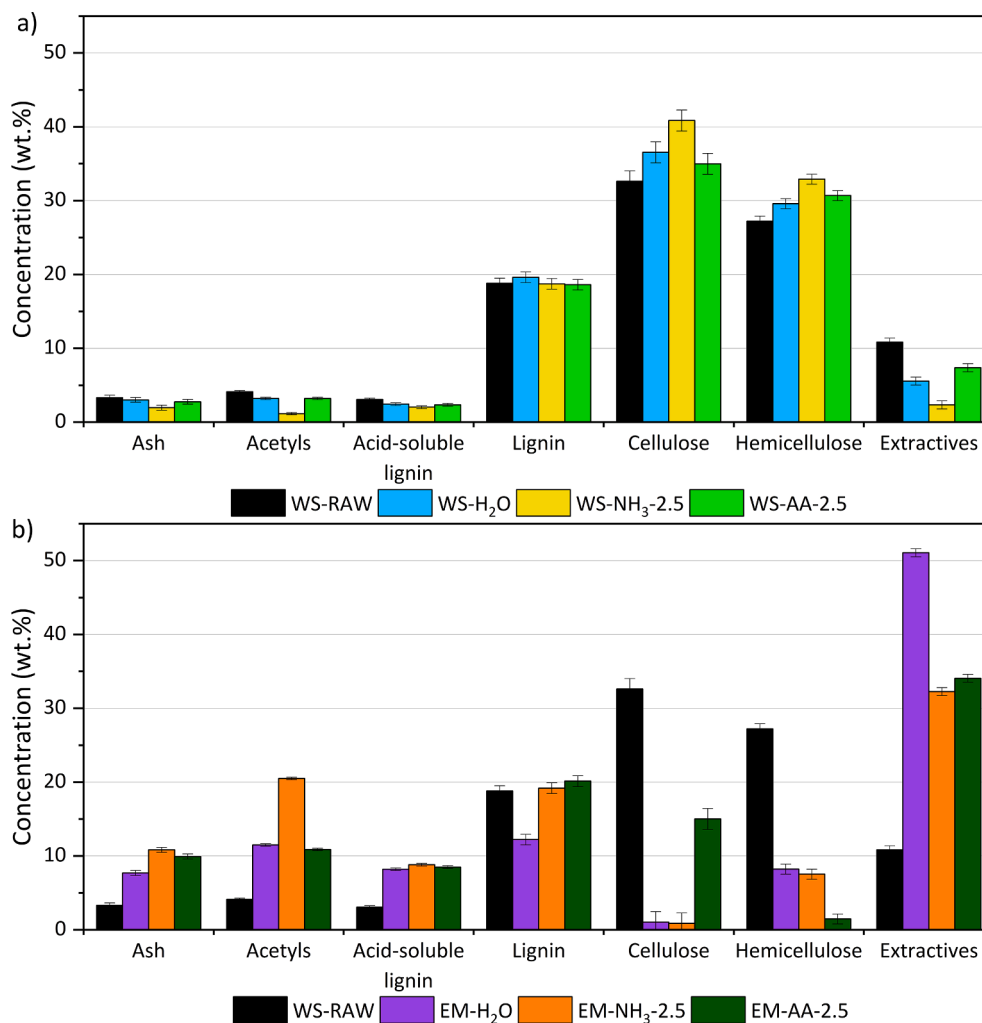


Fig. 3. Components distribution in raw WS, washed WS (a) and EM (b) samples.

pyrolysis tests were carried out using the WS samples washed with water and aqueous solutions of ammonia (2.5 wt%) and acetic acid (2.5 wt%), as well as the corresponding extracted matter, as feedstock. Likewise, a pyrolysis test was performed with the raw wheat straw to be used as a reference.

Reaction yields of the different pyrolysis products (bio-oil*, water, gas, and char) are shown in Fig. 4. Acetic acid pretreatment drastically increases the bio-oil* yield in comparison with the WS-Raw pyrolysis, passing from ca. 35 to 53 wt%. This means that the production of bio-oil* is augmented by a factor of 1.5. In contrast, the yields of the other fractions (water, gas and char) are significantly reduced compared to the test carried out with the raw wheat straw. This remarkable improvement of the bio-oil* yield can be attributed to the changes induced by the acetic acid pretreatment on the biomass composition. In contrast, very different product distribution is obtained when the extracted matter from the acetic acid pretreatment (EM-AA-2.5) is used as feedstock for the pyrolysis test. This sample produces a low amount of bio-oil* (about 20 wt%), generating more char and gases with respect to WS-Raw. These results can be attributed to the high proportion of ash, lignin and extractives that are present in the extracted matter [6,18]. On the other hand, an interesting and surprising finding is that the water yield obtained in the pyrolysis of both samples derived from the acetic acid pretreatment (WS-AA and EM-AA) is lower than that corresponding to the reference pyrolysis test with the initial wheat straw. This fact suggests that dehydration reactions are particularly promoted by the interaction of AAEMs components with the polysaccharides present in

the raw wheat straw, probably through cross-linking condensation reactions that finally result also in the production of additional char. Therefore, separating both components in different fractions by the AA washing treatments reduces significantly the extension of those dehydration reactions, which in turn leads to a decrease in the overall water generation. The bio-oil* yield obtained using the WS sample washed with diluted ammonia is quite similar to that achieved with the acetic acid pretreatment. This fact could be related to a balanced effect of the higher hemicellulose content of WS-NH₃-2.5, which leads to an increase of the organic liquid products, and the slightly higher residual amount of AAEMs that remains in the ammonia-washed sample, promoting the occurrence of bio-oil* conversion reactions.

In the case of the water pretreatment, variations in the pyrolysis product distribution present similar trends to those of the AA and NH₃ washings, although quite less pronounced. Thus, for the WS-H₂O sample the bio-oil* yield is ca. 40 wt%, which represents a slight increase in comparison with that of the WS-Raw (about 35 wt%). In this way, bio-oil*, water and char yield from WS-H₂O pyrolysis are between those of WS-Raw and samples washed with AA and NH₃. These results agree well with the intermediate efficiency of the ash removal, and in particular of AAEMs, achieved with the water pretreatment.

On the other hand, the pyrolysis of the EM-H₂O sample leads to a product distribution quite similar to that of the extracted matter derived from acetic acid pretreatment. Thus, the bio-oil* yield is practically the same for both EM samples (about 19 wt%). The pyrolysis of EM-NH₃-2.5 yields more char, water, and bio-oil* but lower production of non-

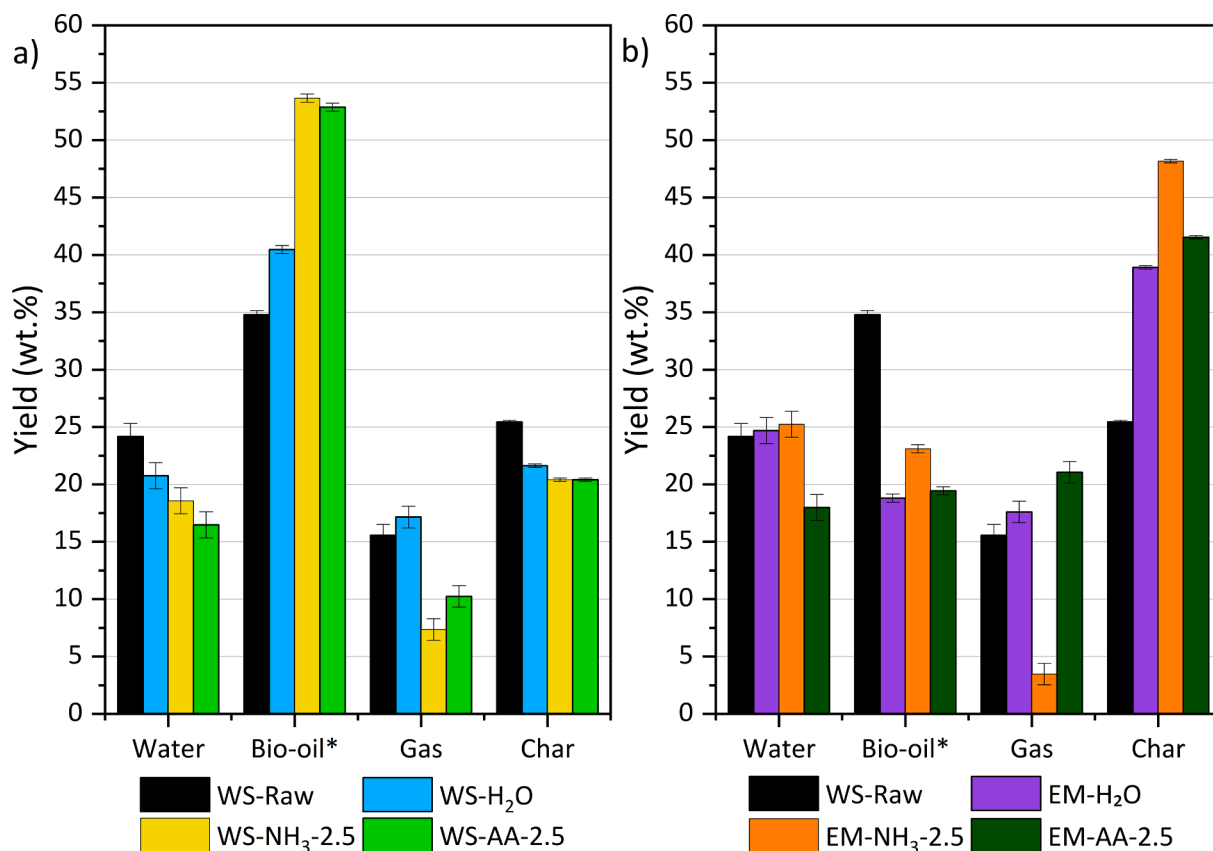


Fig. 4. Pyrolysis product yields of WS-Raw, WS-H₂O, WS-NH₃-2.5, WS-AA-2.5 (a) and WS-Raw, EM-H₂O, EM-NH₃-2.5 and EM-AA-2.5 (b).

condensable gases than EM-AA-2.5 and EM-H₂O, which can be assigned to the higher organic and AAEMs contents, in particular K, in this sample.

Fig. 5 depicts the yield of the main components present in the gaseous stream for all the pyrolysis tests. For the samples pretreated with AA and NH₃, an important reduction in the production of CO and CO₂ occurs in comparison with the raw biomass. In contrast, the sample pretreated with water shows yields of the different gaseous compounds very similar to those of the pyrolysis of the WS-Raw material. On the other hand, some interesting variations can be appreciated in the pyrolysis tests of the EM samples according to the overall gas yields. Thus, for both extracted matters with H₂O and AA, the CO₂ yield increases with respect to the raw biomass but that of CO is reduced. These results suggest that the AAEMs present in the ash fraction are directly involved in promoting decarboxylation reactions over decarboxylation ones [19,22]. In this way, as illustrated in Fig. S2, the CO₂/CO molar ratio is quite higher in the case of the EM pyrolysis in comparison with that of the raw biomass and washed samples.

The elemental composition of all bio-oils* and char samples is shown in Table 3. All pretreatments slightly increase bio-oil* carbon content and reduce oxygen content. Water treatment is the most effective in terms of bio-oil* deoxygenation, which can be linked to the higher CO and CO₂ production. As to the char elemental composition, all washed samples generate a solid residue with more carbon and less oxygen than the one produced from the raw biomass. Therefore, great differences are observed for these feedstock between the elemental composition of the liquid and solid fractions produced during the pyrolysis. However, this is not the case of the extracted matters coming from AA and water washings, in which the differences in the C and O content between the bio-oil* and char products are quite less pronounced. In this way, the chars obtained in the pyrolysis of EM samples contain a relatively large share of oxygen (between ca. 32 – 36 wt%). These results, together with

the high char yield derived from the EM pyrolysis, evidence the difficulty of generating volatile species from these materials. As EM samples accumulate most of the extracted AAEMs, it can be envisaged that the latter largely promote the extension of condensation transformations into high molecular species rather than cracking reactions leading to lighter components [34]. In the case of EM-NH₃, both bio-oil* and char exhibit a lower oxygen content (35.6 and 15.0 wt%, respectively). This fact is related to the significant nitrogen amount present in those phases (12.1 and 4.9 wt%, respectively) as a consequence of the ammonia washing. This effect is accentuated in the resultant biochar due to the higher amount of ash accumulated as a result of the major demineralization efficiency of the NH₃ pretreatment.

The chemical composition of bio-oil is fundamental for the design of downstream processes since it would strongly affect the characteristics of the final desired product. Bio-oil* composition from calibrated GC-MS analysis is shown in Fig. 6, where compounds are grouped in families based on their main functional group.

Washing the biomass with acetic acid reduces the concentration of ketones, ethers and acids, while the concentration of furans, phenols and sugars is enhanced. In particular, the increase of the sugar yield is amazing passing from about 0.5 wt% in the WS-Raw up to ca. 10 wt% in the bio-oil* produced from the AA washed feedstock. This finding can be connected with previous studies about the effects of inorganic metals on the thermal pyrolysis of biomass [33,46]. In fact, the elimination of almost all AAEMs from biomass ashes by acid washing avoids the occurrence of secondary reactions such as ring fission and glucose fragmentation, which are mainly catalyzed by potassium, yielding light oxygenated compounds and gaseous components [6]. Thus, previous studies demonstrated that acetic acid, which represents the 90 wt% of the acids family, can be produced from direct depolymerization and fragmentation of cellulose in the presence of potassium and not only from hemicellulose decomposition [15,47,48].

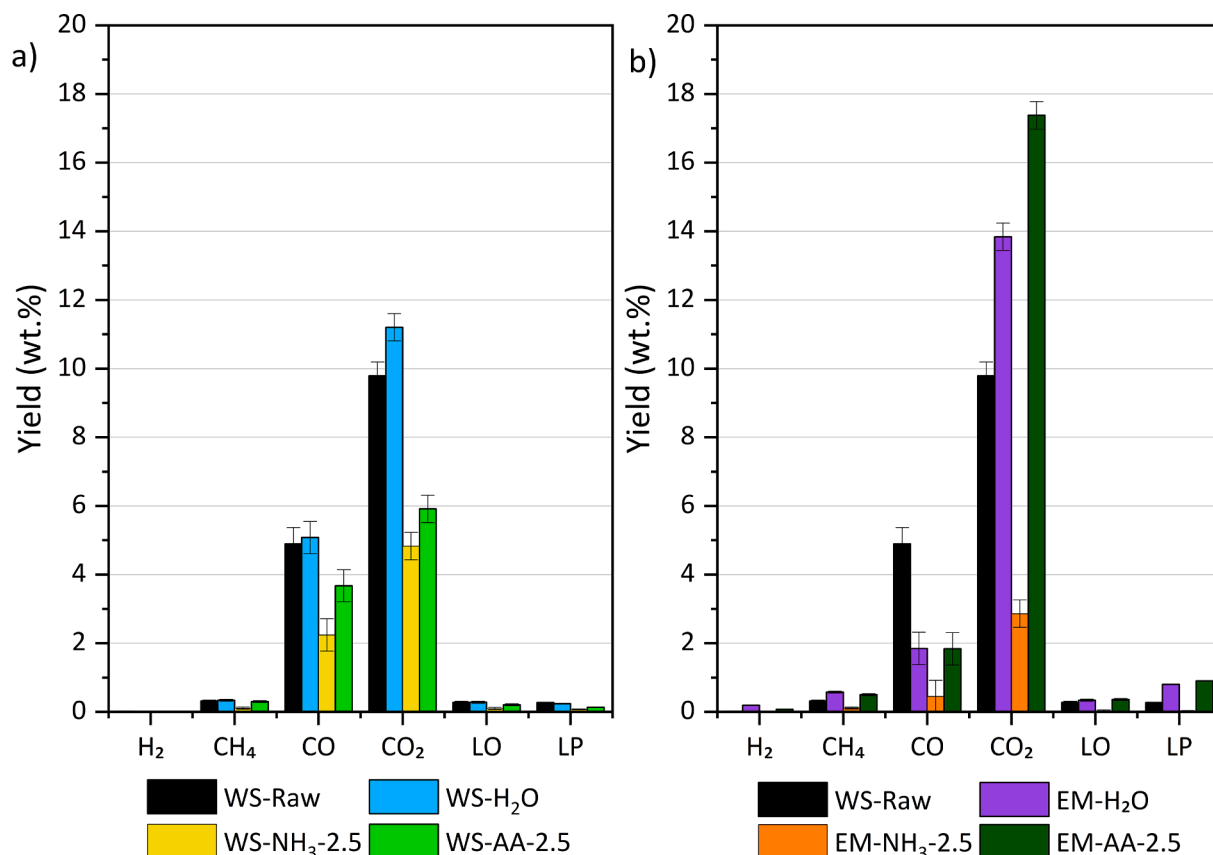


Fig. 5. Gas components yields derived from the pyrolysis of WS-Raw, WS-H₂O, WS-NH₃-2.5 and WS-AA-2.5 (a) and WS-Raw, EM-H₂O, EM-NH₃-2.5 and EM-AA-2.5 (b).

Table 3

Elemental composition of bio-oil* and char samples (wt%).

| | Sample | C | H | N | O | Ash |
|-------------------------|-------------------------|--------|------|------|------|------|
| Bio-oil | WS-Raw | 50.3 | 6.8 | 1.8 | 41.2 | n.a. |
| | WS-H ₂ O | 55.8 | 6.8 | 1.3 | 36.2 | n.a. |
| | EM-H ₂ O | 45.7 | 9.0 | 4.9 | 40.4 | n.a. |
| | WS-NH ₃ -2.5 | 52.4 | 6.6 | 1.1 | 39.8 | n.a. |
| | EM-NH ₃ -2.5 | 42.7 | 9.6 | 12.1 | 35.6 | n.a. |
| | WS-AA-2.5 | 53.1 | 6.2 | 1.1 | 39.6 | n.a. |
| | EM-AA-2.5 | 46.2 | 8.0 | 3.5 | 42.3 | n.a. |
| | Error (±wt.%) | 0.68 | 0.04 | 0.37 | 1.01 | n.a. |
| | Char | WS-Raw | 68.7 | 3.2 | 0.8 | 14.2 |
| WS-H ₂ O | | 71.4 | 2.9 | 0.7 | 10.9 | 14.0 |
| EM-H ₂ O | | 49.0 | 2.4 | 1.4 | 32.4 | 14.8 |
| WS-NH ₃ -2.5 | | 74.8 | 3.3 | 0.8 | 11.1 | 10.1 |
| EM-NH ₃ -2.5 | | 54.0 | 2.9 | 4.9 | 15.0 | 23.1 |
| WS-AA-2.5 | | 72.4 | 3.0 | 0.9 | 10.2 | 13.5 |
| EM-AA-2.5 | | 41.8 | 2.4 | 1.1 | 36.7 | 18.0 |
| Error (±wt.%) | | 0.69 | 0.04 | 0.37 | 0.70 | 0.50 |

The pyrolysis of the biomass washed with water produces a bio-oil* in which yields of the different compound families are intermediate between WS-Raw and WS-AA-2.5, except for carboxylic acids. The yield of the latter family from WS-H₂O is higher than in the case of WS-Raw, while acids yield from WS-AA-2.5 is lower than for WS-Raw. In this case, the increase in the sugars concentration due to water treatment is very low compared to the effect of the AA pretreatment. These results indicate that the presence of a residual AAEMs content in sample WS-H₂O may have a significant and detrimental catalytic activity.

The same conclusion can be drawn from the composition of the bio-oil generated from the sample WS-NH₃-2.5. Thus, despite having the highest holocellulose content, sugars and furans yields are in the middle

of WS-H₂O and WS-AA-2.5 in agreement with the intermediate AAEMs content, especially K and Mg, which contribute to the conversion of those compounds in light oxygenated species, such as ketones and ethers.

On the other hand, the EM samples lead to a bio-oil* that is rich in acetic acid and light oxygenated compounds, agreeing with its high content of acetyls and extractives [49]. In contrast, the yields of sugars and furans are very low since the holocellulose biopolymers are not extracted in significant amounts during the pretreatments but concentrated in the washed samples. In this way, the concentration of oxygenated aromatics is slightly higher than those of sugars and furans, which agrees with the higher share of lignin in EM samples with respect to cellulose and hemicellulose.

Bio-oil* may also contain lignin and cellulose oligomers, as well as other heavy species, that contribute to increase its viscosity and instability over time. Most of these components cannot be detected directly by GC-MS technique [50]. Nonetheless, thanks to an accurate determination of the detected components via internal standard calibration, their overall concentration/yield can be estimated by difference. As shown in Fig. 7, the total bio-oil* detected and identified fraction does not change significantly by washing the biomass, being ca. 50 wt% of the total bio-oil* yield. Since both bio-oil* detected and non-detected fractions are enhanced when total bio-oil* yield increases, it can be deduced that the negative effect of secondary reactions promoted by AAEMs affects both light and heavy components in the bio-oil*. On the other hand, the bio-oil* obtained from the EM samples presents a higher content of heavy and oligomeric species than the raw and washed wheat straw materials, which also denotes the difficulty of transforming these materials into light components.

Product yields, bio-oil* elemental composition and compounds distribution from WS-Raw pyrolysis have been compared with the sum of

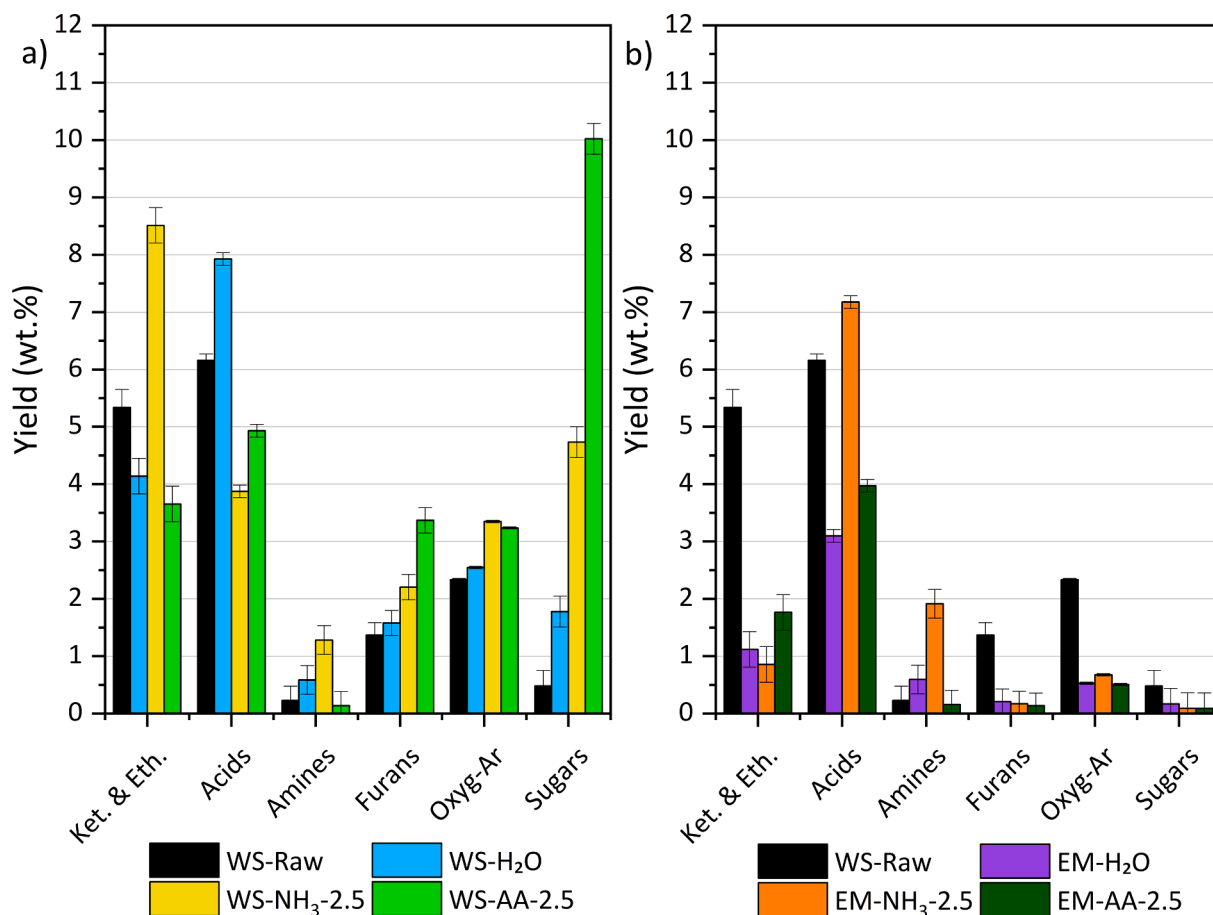


Fig. 6. Molecular composition of bio-oil* samples derived from the pyrolysis of WS-Raw, WS-H₂O, WS-NH₃-2.5 and WS-AA-2.5 (a) and of WS-Raw, EM-H₂O, EM-NH₃-2.5 and EM-AA-2.5 (b).

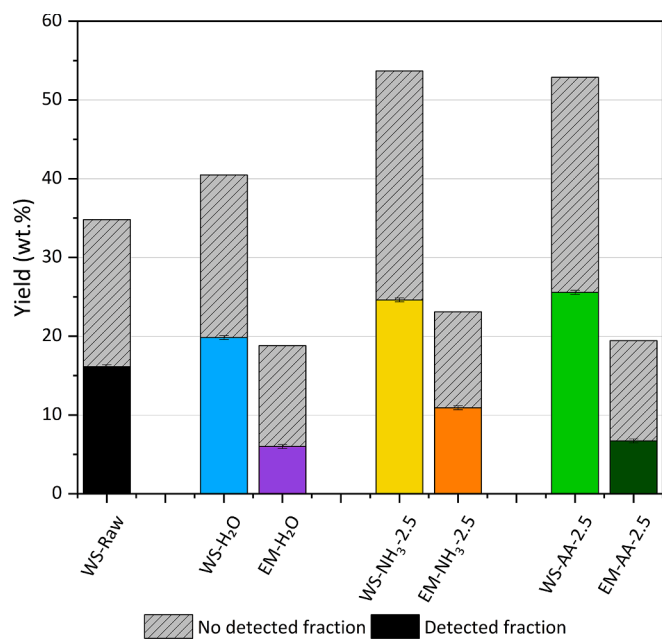


Fig. 7. Overall yield of GC-MS detected and non-detected components in the bio-oil* fractions derived from the pyrolysis of WS-Raw, WS-H₂O, EM-H₂O, WS-NH₃-2.5, EM-NH₃-2.5, WS-AA-2.5 and EM-AA-2.5 samples.

the results obtained for washed WS and EM pyrolysis, weighted on the respective washing yields according to Eq. (4). Results of the calculation are shown in Fig. S3. The weighted addition of the results of WS-H₂O and EM-H₂O pyrolysis does not change significantly in comparison with the values corresponding to WS-Raw. Minor differences include a lower bio-oil* oxygen content and ketones and ethers yield, while bio-oil*, CO₂, acids and sugars yields are slightly higher than those of WS-Raw. In contrast, important differences can be appreciated when comparing the WS-Raw pyrolysis results with the weighted sum of WS-AA-2.5 and EM-AA-2.5. In particular, both total bio-oil* and levoglucosan yields are quite higher in the addition results than those in WS-Raw, while char, gas and water production are lower. The weighted addition of WS-NH₃-2.5 and EM-NH₃-2.5 provides similar results to acetic acid washing in terms of pyrolysis product yields, but the bio-oil* composition is intermediate between samples washed with water and acetic acid. These results confirm that, among the WS washings here investigated, acetic acid pretreatment is the one that most positively affects the pyrolysis of holocellulose components, largely avoiding their interaction with AAEMs species, rather than having a simple additive effect caused by the extraction of biological and inorganic matter. However, this is not the case of lignin since all pretreatments do not almost affect phenols yield when comparing the pyrolysis results of the WS-Raw sample with the weighted addition values. Probably, this is related to the fact that a significant part of the lignin is leached during the washing treatments, being then recovered in the extracted matter.

To illustrate the main conclusions from this section, Fig. 8 depicts how the WS washing pretreatment with acetic acid changes the biomass composition, provoking its speciation into two fractions, which subsequently has remarkable effects on the product distribution derived from

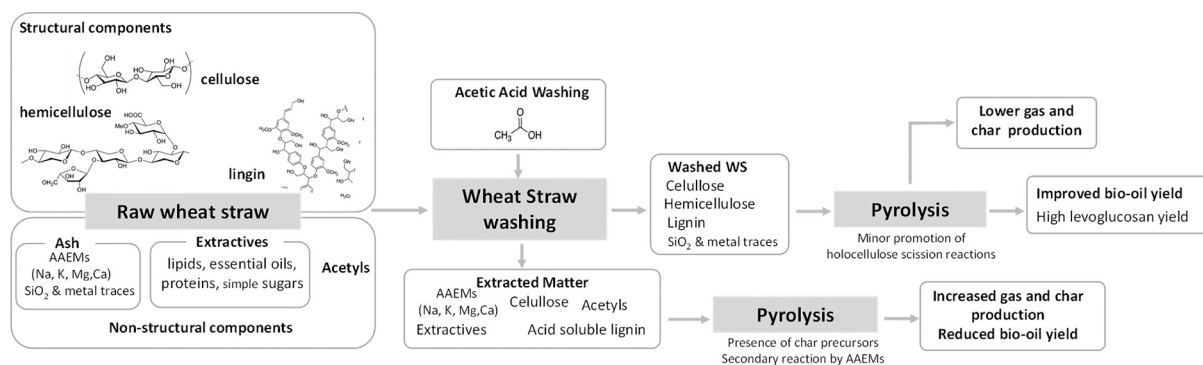


Fig. 8. Scheme of main effects produced by the WS washing pretreatment with AA on both the biomass composition and the product distribution derived from the pyrolysis process.

the pyrolysis process.

3.3. Relationship between the bio-oil* and levoglucosan yields and the AAEMs and polysaccharide contents

Previous results have demonstrated the strong influence of the washing pretreatment of wheat straw on the yields of the pyrolysis product, especially on the bio-oil* production. This fact is related to the efficiency of the washing for the removal of AAEMs species, which are responsible of the occurrence of non-desired secondary reactions [6]. This effect is illustrated in Fig. 9.a, showing that the bio-oil* yield is inversely proportional to the AAEMs content in the WS-Raw, WS-H₂O, WS-NH₃-2.5 and WS-AA-2.5 samples. However, this trend is not followed when comparing the EM samples as in this case the material

derived from the AA treatment presents a slightly higher bio-oil* yield despite having quite more AAEMs content. This apparent anomaly can be explained with Fig. 9.b that denotes also an important correlation between the bio-oil* yield and the holocellulose content of the samples. In fact, for materials with high AAEMs contents and a low share of cellulose and hemicellulose (EM samples), the latter seems to be the limiting factor for the bio-oil* production. This conclusion agrees with the high content of other components (mainly soluble lignin and extractives) present in the EM samples leading mostly to char and gases during the pyrolysis process, as earlier highlighted.

However, the most interesting finding is the correspondence between the AAEMs content in the feedstock and the levoglucosan production, which is especially high when the wheat straw is treated with acetic acid, achieving values close to 10 wt% (Fig. 10). Thus, the almost

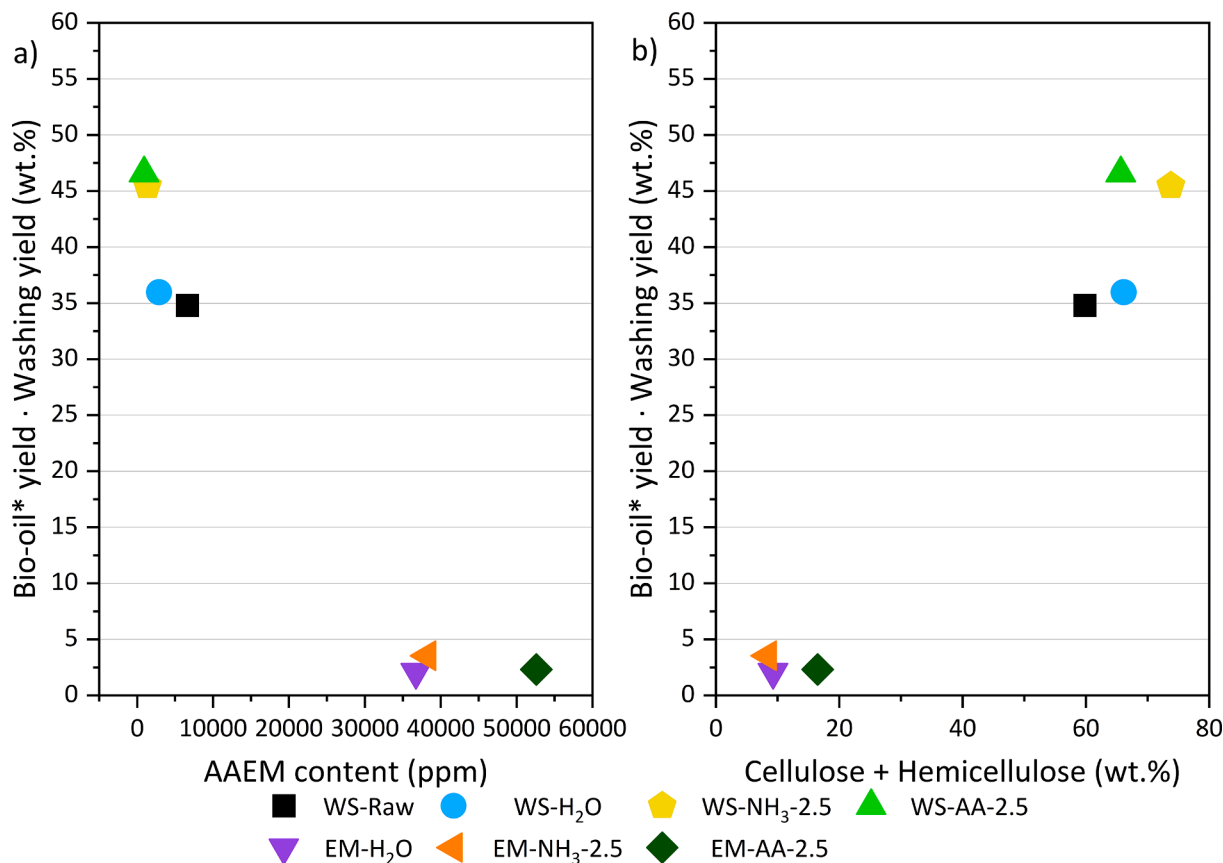


Fig. 9. Bio-oil* yield versus (a) total AAEM content and (b) holocellulose content of raw WS, washed WS and EM samples. Bio-oil yields are calculated considering the washing yields of every WS and EM sample.

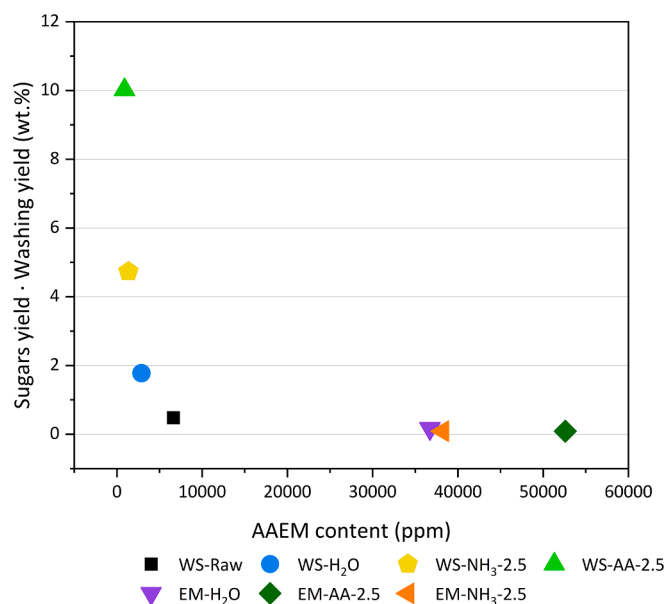


Fig. 10. Levoglucosan* yield versus (a) total AAEM content of raw WS, washed WS and EM samples. (Levoglucosan yields are calculated considering the washing yields of every WS and EM sample).

complete elimination of K, Na, and Mg attained with AA washing significantly reduces the promotion of ring scission reactions, leading to an increased availability of cellulose, which is the main precursor of levoglucosan [51].

3.4. Preliminary study of techno-economic feasibility

In order to complement the previous identified benefits of the wheat straw pretreatment with AA, a preliminary feasibility assessment is addressed in this section, considering technical and economic aspects, by comparison with a reference pyrolysis process using non-pretreated biomass (WS-Raw).

Firstly, an exploratory optimization of the AA washing pretreatment was performed. Thus, the water:biomass mass ratio was progressively reduced to determine the minimum value that allowed the biomass to be properly stirred and suspended. This value was 12:1 w/w. Using this ratio, the AAEMs removal efficiency of solutions with acetic acid

concentrations ranging from 0.25 to 1 wt% were also evaluated. These results are summarized in Table S1 together with those obtained using water and AA solutions of 1 wt% and a water:biomass mass ratio of 20:1 w/w. It can be observed that the washing yield is little affected by the AA concentration neither by the water:biomass mass ratio. However, the same is not observed with the content of AAEMs, which increases when both AA concentration and water:biomass ratio are reduced. Nevertheless, in all cases, the AAEMs contents are clearly lower than those obtained using pure water as washing agent. In this sense, washing with a solution of 0.75 wt% of acetic acid, the AAEMs removal, washing yields and ash content in the WS were quite close to those attained with higher AA concentrations. Accordingly, the solution of 0.75 wt% of AA with a water:biomass ratio of 12:1 w/w was selected for this preliminary feasibility study as these conditions involve a smaller need of AA as well as lower consumption of energy for filtering and drying stages that should be carried out before the pyrolysis process.

Using this sample (WS-AA-0.75) as feedstock, an additional pyrolysis assay was carried out to determine the experimental data required for this study. Table S2 summarizes the yields and composition of the pyrolysis products, as well as the levoglucosan production obtained under these conditions. These results denote that using these washing conditions also improves significantly both the bio-oil* and levoglucosan yields regarding the reference case (pyrolysis of WS-raw).

Fig. 11 (a and b) presents the process diagram considered for both the WS-raw and WS-AA-0.75 pyrolysis processes. In both cases, the capacity of the plant has been set at 300,000 tons of raw wheat straw per year, operating 8000 h a year.

In the conventional process, raw wheat straw (15 wt% moisture [52]) is firstly milled to reduce the particle size, dried up to 7 wt% moisture and fed to the pyrolysis reactor at 550 °C. The product fractions from pyrolysis (gases, bio-oil and char) are then separated, and the gas fraction and part of the char are considered to be burnt to satisfy the heat requirement in the pyrolysis operation. The leaving exhaust gases, at 700 °C, are used to provide the thermal needs in the biomass dryer. The main results of this process, including material and energy balances, are detailed in Table 4.

The process involving acetic acid WS pretreatment also begins with the milling of the biomass. After reducing the particle size, the WS undergoes the extraction operation with an aqueous solution of acetic acid (AA, 0.75 wt%), being washed with water to adjust pH to neutral conditions. As a consequence of these operations, around 12 wt% of the dry biomass mass is dragged with the extractive solution and water, mainly comprising ash and extractive organic compounds. On the contrary, the

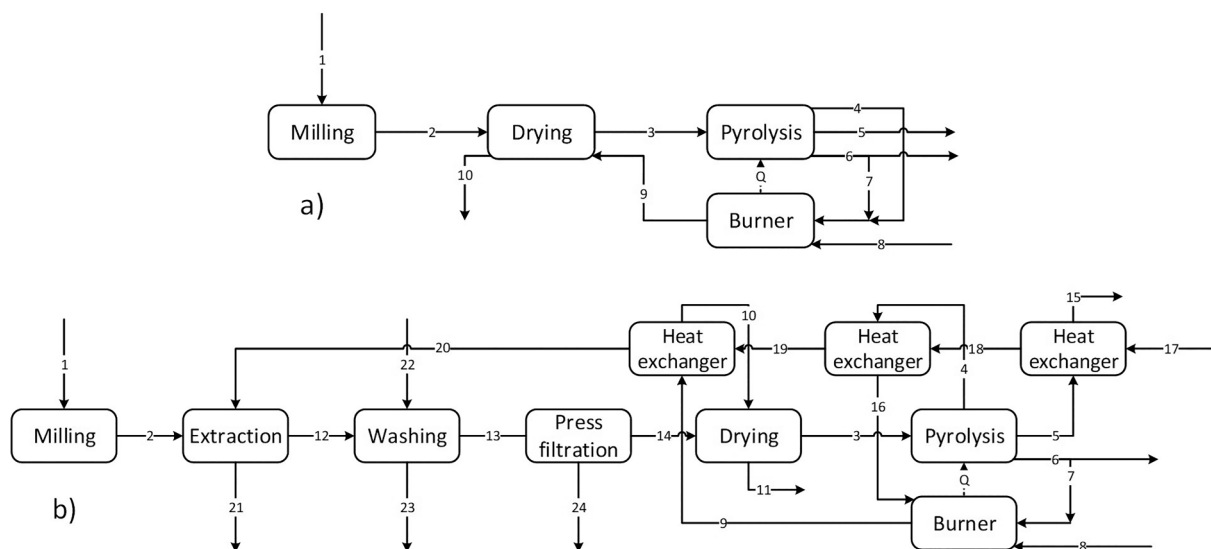


Fig. 11. Process diagram of (a) reference pyrolysis process (WS-raw) and (b) pyrolysis process considering WS pretreatment with AA washing (WS-AA-0.75).

Table 4

Summary of material and energy balances of main influenced items for WS-raw and WS-AA-0.75 processes.

| Material balance | WS-raw | | | WS-AA-0.75 | | Comment | |
|-------------------------------|--------|--------|------------------|-----------------|------------------|---------|---|
| | Stream | T (°C) | Mass flow (kg/h) | Moisture (wt.%) | Mass flow (kg/h) | | Moisture (wt.%) |
| | 1 | 25 | 37,500 | 15.0 | 37,500 | 15.0 | Raw biomass |
| | 2 | 25 | 37,500 | 15.0 | 37,500 | 15.0 | Milled biomass |
| | 3 | 80 | 34,270 | 7.0 | 30,250 | 7.0 | Dried biomass |
| | 4 | 550 | 5312 | 0.0 | 2977 | 0.0 | Gas fraction; LHV = 5.99 MJ/kg in base case; LHV = 6.79 MJ/kg in extraction case |
| | 5 | 550 | 20,048 | 40.2 | 20,764 | 29.0 | Bio-oil fraction; LG = 0.9 wt%, AA = 11.9 wt% in base case; LG = 9.6 wt%, AA = 5.3 wt% in extraction case |
| | 6 | 550 | 8910 | 0.0 | 6510 | 0.0 | Char fraction; LHV = 26.9 MJ/kg |
| | 14 | 25 | - | - | 49,232 | 42.9 | Pressed wet biomass |
| | 20 | 50 | - | - | 450,000 | - | Water (99.25 wt%) + AA (0.75 wt%) |
| Energy balance | | | | | | | |
| Heat pyrolysis (GJ/h) | | | 34.1 | | 30.1 | | |
| Heat dryer (GJ/h) | | | 8.3 | | 48.8 | | |
| Heat extraction (GJ/h) | | | - | | 43.7 | | |
| Potential heat - gases (GJ/h) | | | -31.8 | | -20.2 | | Based on LHV |
| Potential heat - char (GJ/h) | | | -239.8 | | -175.2 | | Based on LHV |
| Power | | | | | | | |
| Power filtration (MW) | | | - | | 1.2 | | |
| Agitator extraction (MW) | | | - | | 0.6 | | |

biomass undergoes a weight gain in terms of water content, thus being required a subsequent step of press filtering to eliminate it. After this operation, the biomass reaches a moisture content of approximately 43 wt% (observed experimentally), next entering the dryer to reduce it up to 7 wt% and being fed to the pyrolysis reactor at 550 °C. Thereafter, the product from the pyrolysis (gases, bio-oil and char) are separated, and bio-oil and gas fractions are used to preheat the inlet AA solution in respective heat exchangers. Again, pyrolysis gases and part of the char are considered to be burnt to satisfy the heat requirement in the pyrolysis operation, and the exhaust gases, at 700 °C, are used to heat up the AA solution to the required temperature of the extraction (50 °C) and to provide the remaining heat in the drying step. The main results of this process are also collected in Table 4.

Comparing the assessed processes, it is observed a decrease in the production of gases and char yields in favor of the bio-oil* yield for the WS-AA-0.75 case (+2740 kg/h). Despite the decrease in the gas phase

production, the quality of this fraction is improved as higher LHV is obtained. On the other hand, besides the enhancement of bio-oil* yield, the content of levoglucosan (LG) increases significantly, which is a high-added value chemical [53]. However, it is found some reduction in the AA production, which is assumed to be potentially recirculated to the extraction process, thus lowering the consumption of fresh AA, previous separation and purification.

On the other hand, the heat consumption is increased when the AA washing pretreatment is performed, principally due to the WS drying operation. Nonetheless, considering the produced amounts of gases and char, as well as their LHV, there is enough chemical energy available to satisfy the required heat, thus demonstrating its potential self-sufficiency. Additionally, power consumption results higher when compared to the WS-raw case, mainly associated with the extraction and filtration steps, which directly influences the economic balance.

Regarding the preliminary economic feasibility of the pretreatment, Table 5 summarizes the main figures in terms of production costs difference between both options, i.e. the extra cost or savings for each item of the WS-AA-0.75 process relative to the reference WS-Raw process. As can be observed, costs associated with fresh AA and extra power consumption are higher with the pretreatment (+9069 and +999 k€/y, respectively), as well as capital costs associated with equipment of the related operations (i.e. extraction tank, agitator, filter, heat exchangers and increase on the dryer capacity). On the other hand, capital costs derived from the pyrolysis reactor are reduced (-148 k€) since its capacity also decreases, while potential incomes from the enhanced production of bio-oil* and, especially, levoglucosan contribute to tilt the balance to an economically feasible scenario (+3695 and +48526 k€/y, respectively). Indeed, a final reduction of 43237 k€/year in the costs is found for the WS-AA-0.75 case compared with WS-raw case, which potentially indicates a feasible and better economic scenario for the biomass pretreatment.

It is important to note that the economic results are strongly influenced by the LG price, which is difficult to be estimated due to the lack of reliable data at industrial scale. It has been reported that the LG price may vary in a wide range (10 – 50 \$/kg) [55]. On the other hand, some recent works have concluded that the production costs for LG could be set from 1.3 \$/kg to 4.5 \$/kg [53,55]. Taking into account these figures, in the current work, a conservative value of the LG selling price of 3.3 \$/kg has been considered. Despite this value being lower than other reported selling prices, a remarkable economic improvement is obtained regarding the reference process. Nevertheless, it must be taken into consideration that these are preliminary results and further research would be required in a number of aspects, like the optimization of the operations for the AA recovery from the bio-oil and the possibility of

Table 5

Summary of preliminary economic implications of WS-AA-0.75 process compared to WS-raw.

| | Unit price | Increment yearly cost (k€/y) | Comments |
|------------------------|-------------|------------------------------|-----------------------|
| AA | 500 €/t | 9,069.1 | from [54] |
| LG ¹ | 3300 \$/t | -48,526.4 | from [55] |
| BO* (-LG) ² | 200 €/t | -3,694.7 | from [56] |
| Power | 115.2 €/MWh | 999.1 | EU-2019S2 from [57] |
| Equipment ³ | k€ | | |
| Pyr. Reactor | -148.4 | -14.8 | from [56] |
| Ext. tank | 269.9 | 27.0 | calculated as in [58] |
| Exchangers | 117.7 | 11.8 | calculated as in [58] |
| Agitator | 331.5 | 33.2 | from [59] |
| Dryer | 289.9 | 29.0 | from [60] |
| Filter | 127.7 | 12.8 | from [61] |
| Total | | -43,237.1 | |

¹LG: levoglucosan.

²BO* (-LG): bio-oil on a water-free basis without levoglucosan.

³Capital costs related to equipment has been annualized assuming a linear amortization of 10 years.

reusing the AA washing solution to reduce the input of fresh AA. In any case, results in the literature are in line with this work, reporting techno-economic feasibility of processes producing LG from biomass, which contributes to prove the benefits of this type of pretreatment process in biomass pyrolysis [53,55,61,62].

4. Conclusions

Wheat straw can be effectively demineralized by washing with diluted acetic acid solutions, showing removal rates of Na, K, Mg, and Ca much higher than those achieved by pretreatment with water or diluted NH₃. In addition, these three reagents partially dissolve the organic fraction (between ca. 11 and 14 wt% of the raw biomass), inducing significant changes in the composition and contents of the biopolymers (cellulose, hemicellulose and lignin) and other non-structural components (extractives, acetyls, etc). Thus, washed samples showed a lower percentage of fixed carbon and a higher proportion of holocellulose, while soluble lignin and extractives are concentrated in the extracted matter.

These modifications in the composition and structure of the raw biomass, caused by the washing pretreatments, have important impacts on the product distribution obtained in a subsequent pyrolysis process. Interestingly, the bio-oil* (bio-oil in dry basis) yield was significantly increased, passing from 35 wt% when the raw wheat straw is used as feedstock up to 53 wt% in the case of the biomass sample washed with acetic acid. In addition, acetic acid pretreatment lowered the formation of the other fractions (char, water and gases). Relevant changes are also observed in the bio-oil* composition, with a reduction in the concentration of aldehydes, ketones, and carboxylic acids and a sharp enhancement in the production of furans, and especially of levoglucosan (yield over 10 wt%), which becomes the main component of the bio-oil* fraction. Ammonia has a stronger effect than acetic acid in extracting and dissolving both organic and inorganic matter, resulting in a washed biomass with the highest holocellulose content, but not in terms of AAEMs extraction. As a result, pyrolysis product yields obtained from the biomass washed with NH₃ are similar to that washed with AA, but the bio-oil* quality is not enhanced to the same extent since levoglucosan and furans production is much lower.

In contrast, pyrolysis of the extracted matter samples, recovered from the washing solutions, leads to quite larger production of char, yielding also more gases and rather less bio-oil* than the raw wheat straw. Likewise, the bio-oil* obtained from the EM samples presents a higher content of heavy and oligomeric species than the raw and washed wheat straw materials.

Considering together the results obtained in the pyrolysis of all materials (raw, washed and extracted matter samples), it is concluded that the production of high bio-oil* yields can be linked not only to the removal of AAEMs species, thus avoiding undesired secondary reactions, but also with the increase of the share of holocellulose components, which are the main precursors of both furans and anhydrosugars.

In summary, acetic acid washing is a promising pretreatment to improve the quantity and quality of the bio-oil* produced by pyrolysis. In this way, pretreatment with acetic acid in diluted solutions is as effective as the use of strong acids, extensively investigated in the literature, for the deashing of this kind of agricultural residues. Additionally, acetic acid is a biodegradable, non-toxic and non-polluting solvent and can be produced through biomass pyrolysis, leading to a self-sustained process. Finally, a preliminary study of techno-economic feasibility found that wheat straw washing with acetic acid can significantly improve the economic performance of the process since the enhanced bio-oil* and, in particular, levoglucosan yields generate remarkable additional revenues that compensate the extra-costs associated with the pretreatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The present work received funding from the Spanish Ministry of Science and Innovation under the grant PID2020-114740RB-C21 (ADBIOCAP Project). The authors also would like to acknowledge CIE-MAT Institute, and in particular Dr. Ignacio Ballesteros from the Renewable Energy Department, for carrying out the analysis to determine the biopolymers composition of all biomass samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.140206>.

References

- [1] Y. Makarfi Isa, E.T. Ganda, Bio-oil as a potential source of petroleum range fuels, *Renew. Sustain. Energy Rev.* 81 (2018) 69–75, <https://doi.org/10.1016/j.rser.2017.07.036>.
- [2] Y. Wang, A. Akbarzadeh, L. Chong, J. Du, N. Tahir, M.K. Awasthi, Catalytic pyrolysis of lignocellulosic biomass for bio-oil production: A review, *Chemosphere* 297 (2022), 134181, <https://doi.org/10.1016/j.chemosphere.2022.134181>.
- [3] N. Dahmen, I. Lewandowski, S. Zibek, A. Weidtmann, Integrated lignocellulosic value chains in a growing bioeconomy: Status quo and perspectives, *GCB Bioenergy* 11 (2019) 107–117, <https://doi.org/10.1111/gcbb.12586>.
- [4] J. Rajesh Banu, Preethi, S. Kavitha, V.K. Tyagi, M. Gunasekaran, O.P. Karthikeyan, G. Kumar, Lignocellulosic biomass based biorefinery: A successful platform towards circular bioeconomy, *Fuel* 302 (2021) 121086, <https://doi.org/10.1016/j.fuel.2021.121086>.
- [5] A. Thorenz, L. Wietschel, D. Stindt, A. Tuma, Assessment of agroforestry residue potentials for the bioeconomy in the European Union, *J. Clean. Prod.* 176 (2018) 348–359, <https://doi.org/10.1016/j.jclepro.2017.12.143>.
- [6] F.X. Collard, J. Blin, A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin, *Renew. Sustain. Energy Rev.* 38 (2014) 594–608, <https://doi.org/10.1016/j.rser.2014.06.013>.
- [7] I.Y. Eom, K.H. Kim, J.Y. Kim, S.M. Lee, H.M. Yeo, I.G. Choi, J.W. Choi, Characterization of primary thermal degradation features of lignocellulosic biomass after removal of inorganic metals by diverse solvents, *Bioresour. Technol.* 102 (2011) 3437–3444, <https://doi.org/10.1016/j.biortech.2010.10.056>.
- [8] D.M. Keown, G. Favas, J.I. Hayashi, C.Z. Li, Volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass: differences between sugar cane bagasse and cane trash, *Bioresour. Technol.* 96 (2005) 1570–1577, <https://doi.org/10.1016/j.biortech.2004.12.014>.
- [9] S. Zhong, B.o. Zhang, C. Liu, A. Shujaa aldeen, S. Mwenya, H. Zhang, A minireview on catalytic fast co-pyrolysis of lignocellulosic biomass for bio-oil upgrading via enhancing monocyclic aromatics, *J. Anal. Appl. Pyrolysis* 164 (2022) 105544, <https://doi.org/10.1016/j.jaap.2022.105544>.
- [10] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass Bioenergy* 38 (2012) 68–94, <https://doi.org/10.1016/j.biombioe.2011.01.048>.
- [11] R.I. Urrutia, V.S. Gutierrez, N. Stefanazzi, M.A. Volpe, J.O. Werdin González, Pyrolysis liquids from lignocellulosic biomass as a potential tool for insect pest management: A comprehensive review, *Ind. Crops Prod.* 177 (2022), 114533, <https://doi.org/10.1016/j.indcrop.2022.114533>.
- [12] X. Hu, M. Gholizadeh, Progress of the applications of bio-oil, *Renew. Sustain. Energy Rev.* 134 (2020), 110124, <https://doi.org/10.1016/j.rser.2020.110124>.
- [13] H. Hernando, J. Feroso, C. Ochoa-Hernández, M. Opanasenko, P. Pizarro, J. M. Coronado, J. Čejka, D.P. Serrano, Performance of MCM-22 zeolite for the catalytic fast-pyrolysis of acid-washed wheat straw, *Catal. Today* 304 (2018) 30–38, <https://doi.org/10.1016/j.cattod.2017.09.043>.
- [14] S. Hameed, A. Sharma, V. Pareek, H. Wu, Y. Yu, A review on biomass pyrolysis models: Kinetic, network and mechanistic models, *Biomass Bioenergy* 123 (2019) 104–122, <https://doi.org/10.1016/j.biombioe.2019.02.008>.
- [15] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Influence of inorganic salts on the primary pyrolysis products of cellulose, *Bioresour. Technol.* 101 (2010) 4646–4655, <https://doi.org/10.1016/j.biortech.2010.01.112>.

- [16] D. Chen, D. Gao, S. Huang, S.C. Capareda, X. Liu, Y. Wang, T. Zhang, Y. Liu, W. Niu, Influence of acid-washed pretreatment on the pyrolysis of corn straw: A study on characteristics, kinetics and bio-oil composition, *J. Anal. Appl. Pyrolysis* 155 (2021), 105027, <https://doi.org/10.1016/J.JAAP.2021.105027>.
- [17] I.Y. Eom, J.Y. Kim, S.M. Lee, T.S. Cho, H. Yeo, J.W. Choi, Comparison of pyrolytic products produced from inorganic-rich and demineralized rice straw (*Oryza sativa* L.) by fluidized bed pyrolyzer for future biorefinery approach, *Bioresour. Technol.* 128 (2013) 664–672, <https://doi.org/10.1016/J.BIORTECH.2012.09.082>.
- [18] Z. Wang, Q. Wang, X. Yang, S. Xia, A. Zheng, K. Zeng, Z. Zhao, H. Li, S. Sobek, S. Werle, Comparative assessment of pretreatment options for biomass pyrolysis: linking biomass compositions to resulting pyrolysis behaviors, kinetics, and product yields, *Energy Fuels* 35 (2021) 3186–3196, <https://doi.org/10.1021/acs.energyfuels.0c04186>.
- [19] H. Persson, W. Yang, Catalytic pyrolysis of demineralized lignocellulosic biomass, *Fuel* 252 (2019) 200–209, <https://doi.org/10.1016/J.FUEL.2019.04.087>.
- [20] D. Mourant, Z. Wang, M. He, X.S. Wang, M. Garcia-Perez, K. Ling, C.Z. Li, Mallee wood fast pyrolysis: Effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil, *Fuel* 90 (2011) 2915–2922, <https://doi.org/10.1016/J.FUEL.2011.04.033>.
- [21] D.M. Keown, J.-I. Hayashi, C.-Z. Li, Effects of volatile-char interactions on the volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass, *Fuel* 87 (7) (2008) 1187–1194, <https://doi.org/10.1016/J.FUEL.2007.05.056>.
- [22] W. Wang, R. Lemaire, A. Bensakhria, D. Luart, Review on the catalytic effects of alkali and alkaline earth metals (AAEMs) including sodium, potassium, calcium and magnesium on the pyrolysis of lignocellulosic biomass and on the co-pyrolysis of coal with biomass, *J. Anal. Appl. Pyrolysis* 163 (2022), 105479, <https://doi.org/10.1016/J.JAAP.2022.105479>.
- [23] L. Jiang, Y. Wang, L. Dai, Z. Yu, Q. Yang, S. Yang, D. Jiang, Z. Ma, Q. Wu, B. Zhang, Y. Liu, R. Ruan, Co-pyrolysis of biomass and soapstock in a downdraft reactor using a novel ZSM-5/SiC composite catalyst, *Bioresour. Technol.* 279 (2019) 202–208, <https://doi.org/10.1016/J.BIORTECH.2019.01.119>.
- [24] X. Zhang, H. Ma, S. Wu, W. Jiang, W. Wei, M. Lei, Fractionation of pyrolysis oil derived from lignin through a simple water extraction method, *Fuel* 242 (2019) 587–595, <https://doi.org/10.1016/J.FUEL.2019.01.083>.
- [25] R.J.M. Westerhof, D. Wim, F. Brilman, M. Garcia-Perez, Z. Wang, S.R. Oudenhoven, W.P.M. van Swaaij, S.R.A. Kersten, Fractional condensation of biomass pyrolysis vapors, *Energy Fuels* 25 (2011) 1817–1829, <https://doi.org/10.1021/ef2000322>.
- [26] B. Saha, S.P. Chopade, S.M. Mahajani, Recovery of dilute acetic acid through esterification in a reactive distillation column, *Catal. Today* 60 (2000) 147–157, [https://doi.org/10.1016/S0920-5861\(00\)00326-6](https://doi.org/10.1016/S0920-5861(00)00326-6).
- [27] S. Ren, X.P. Ye, A.P. Borole, Separation of chemical groups from bio-oil water-extract via sequential organic solvent extraction, *J. Anal. Appl. Pyrolysis* 123 (2017) 30–39, <https://doi.org/10.1016/J.JAAP.2017.01.004>.
- [28] A. Teella, G.W. Huber, D.M. Ford, Separation of acetic acid from the aqueous fraction of fast pyrolysis bio-oils using nanofiltration and reverse osmosis membranes, *J. Memb. Sci.* 378 (2011) 495–502, <https://doi.org/10.1016/J.MEMSCI.2011.05.036>.
- [29] B. Sukhbatara, P.H. Steele, L. Ingram, M. Kim, An exploratory study on the removal of acetic acid and formic acids from bio-oil, *Bio Resour.* 4 (2009) 1319–1329. https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_04_4_Sukhbatara_SIK_Eval_Removal_Acetic_Formic_Acids_BioOil.
- [30] L. Jiang, S. Hu, L.-S. Sun, S. Su, K. Xu, L.-m. He, J. Xiang, Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass, *Bioresour. Technol.* 146 (2013) 254–260, <https://doi.org/10.1016/J.BIORTECH.2013.07.063>.
- [31] Karnowo, Z.F. Zahara, S. Kudo, K. Norinaga, J.-I. Hayashi, Leaching of alkali and alkaline earth metallic species from rice husk with bio-oil from its pyrolysis, *Energy Fuels* 28 (10) (2014) 6459–6466, <https://doi.org/10.1021/ef501748h>.
- [32] S.D. Stefanidis, E. Heracleous, D.T. Patiaka, K.G. Kalogiannis, C.M. Michailof, A. A. Lappas, Optimization of bio-oil yields by demineralization of low quality biomass, *Biomass Bioenergy* 83 (2015) 105–115, <https://doi.org/10.1016/J.BIOMBIOE.2015.09.004>.
- [33] J. Feroso, H. Hernando, S. Jiménez-Sánchez, A.A. Lappas, E. Heracleous, P. Pizarro, J.M. Coronado, D.P. Serrano, Bio-oil production by lignocellulose fast-pyrolysis: Isolating and comparing the effects of indigenous versus external catalysts, *Fuel Process. Technol.* 167 (2017) 563–574, <https://doi.org/10.1016/J.FUPROC.2017.08.009>.
- [34] S. Zhou, Y. Xue, J. Cai, C. Cui, Z. Ni, Z. Zhou, An understanding for improved biomass pyrolysis: Toward a systematic comparison of different acid pretreatments, *Chem. Eng. J.* 411 (2021), 128513, <https://doi.org/10.1016/J.CEJ.2021.128513>.
- [35] M.J. Negro, C. Álvarez, P. Doménech, R. Iglesias, I. Ballesteros, Sugars production from municipal forestry and greening wastes pretreated by an integrated steam explosion-based process, *Energies* 13 (17) (2020), <https://doi.org/10.3390/en13174432>.
- [36] H. Hernando, S. Jiménez-Sánchez, J. Feroso, P. Pizarro, J.M. Coronado, D. P. Serrano, Assessing biomass catalytic pyrolysis in terms of deoxygenation pathways and energy yields for the efficient production of advanced biofuels, *Catal. Sci. Technol.* 6 (2016) 2829–2843, <https://doi.org/10.1039/C6CY00522E>.
- [37] H. Hernando, A.M. Hernández-Giménez, C. Ochoa-Hernández, P.C.A. Bruijninx, K. Houben, M. Baldus, P. Pizarro, J.M. Coronado, J. Feroso, J. Čejka, B. M. Weckhuysen, D.P. Serrano, Engineering the acidity and accessibility of the zeolite ZSM-5 for efficient bio-oil upgrading in catalytic pyrolysis of lignocellulose, *Green Chem.* 20 (2018) 3499–3511, <https://doi.org/10.1039/C8GC01722K>.
- [38] A. Lago, H. Hernando, J.M. Moreno, D.P. Serrano, J. Feroso, Valorisation of a lignin-rich residue via catalytic pyrolysis over ZrO₂/ZSM-5 technical catalyst, *Fuel Process. Technol.* 215 (2021), 106746, <https://doi.org/10.1016/J.FUPROC.2021.106746>.
- [39] S.D. Stefanidis, K.G. Kalogiannis, E.F. Iliopoulou, A.A. Lappas, P.A. Pilavachi, In-situ upgrading of biomass pyrolysis vapors: Catalyst screening on a fixed bed reactor, *Bioresour. Technol.* 102 (2011) 8261–8267, <https://doi.org/10.1016/J.BIORTECH.2011.06.032>.
- [40] C. Wang, Q. Hao, D. Lu, Q. Jia, G. Li, B. Xu, Production of light aromatic hydrocarbons from biomass by catalytic pyrolysis, *Chinese, J. Catal.* 29 (2008) 907–912, [https://doi.org/10.1016/S1872-2067\(08\)60073-X](https://doi.org/10.1016/S1872-2067(08)60073-X).
- [41] S. Li, C. Wang, Z. Luo, X. Zhu, Investigation on the catalytic behavior of alkali metals and alkaline earth metals on the biomass pyrolysis assisted with real-time monitoring, *Energy Fuels* 34 (2020) 12654–12664, <https://doi.org/10.1021/acs.energyfuels.0c01938>.
- [42] H. Persson, T. Han, L. Sandström, W. Xia, P. Evangelopoulos, W. Yang, Fractionation of liquid products from pyrolysis of lignocellulosic biomass by stepwise thermal treatment, *Energy* 154 (2018) 346–351, <https://doi.org/10.1016/J.ENERGY.2018.04.150>.
- [43] P. Pawar, S. Koutaniemi, M. Tenkanen, E. Mellerowicz, Acetylation of woody lignocellulose: significance and regulation, *Front. Plant Sci.* 4 (2013), <https://doi.org/10.3389/fpls.2013.00118>.
- [44] S. Yasuda, K. Fukushima, A. Kakehi, Formation and chemical structures of acid-soluble lignin I: sulfuric acid treatment time and acid-soluble lignin content of hardwood, *J. Wood Sci.* 47 (2001) 69–72, <https://doi.org/10.1007/BF00776648>.
- [45] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, T.J. Morgan, An overview of the organic and inorganic phase composition of biomass, *Fuel* 94 (2012) 1–33, <https://doi.org/10.1016/J.FUEL.2011.09.030>.
- [46] I.Y. Eom, J.Y. Kim, T.S. Kim, S.M. Lee, D. Choi, I.G. Choi, J.W. Choi, Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass, *Bioresour. Technol.* 104 (2012) 687–694, <https://doi.org/10.1016/J.BIORTECH.2011.10.035>.
- [47] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Product distribution from fast pyrolysis of glucose-based carbohydrates, *J. Anal. Appl. Pyrolysis* 86 (2009) 323–330, <https://doi.org/10.1016/J.JAAP.2009.08.007>.
- [48] D.J. Nowakowski, J.M. Jones, Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds, *J. Anal. Appl. Pyrolysis* 83 (2008) 12–25, <https://doi.org/10.1016/J.JAAP.2008.05.007>.
- [49] X.J. Guo, S.R. Wang, K.G. Wang, Q. Liu, Z.Y. Luo, Influence of extractives on mechanism of biomass pyrolysis, *J. Fuel Chem. Technol.* 38 (2010) 42–46, [https://doi.org/10.1016/S1872-5813\(10\)60019-9](https://doi.org/10.1016/S1872-5813(10)60019-9).
- [50] F. Collard, M. Cooke-Willis, D. van de Pas, K. Torr, Optimising ex-situ catalytic fast pyrolysis of pine wood at pilot scale: Impacts on the energy content, chemical composition and stability of the liquid fuel product, *J. Anal. Appl. Pyrolysis* 168 (2022), 105725, <https://doi.org/10.1016/J.JAAP.2022.105725>.
- [51] E.G. Silveira Junior, T.d.C. Silveira, V.H. Perez, O.R. Justo, G.F. David, S. A. Fernandes, Fast pyrolysis of elephant grass: Intensification of levoglucosan yield and other value-added pyrolytic by-products, *J. Energy Inst.* 101 (2022) 254–264, <https://doi.org/10.1016/J.JOIEI.2022.02.003>.
- [52] ECN, Phyllis2 – Database for the physico-chemical composition of (treated) lignocellulosic biomass, micro- and macroalgae, various feedstocks for biogas production and biochar, *Energy Res. Cent. Netherlands*. (2012) 2–4. <https://phyllis.nl/Browse/Standard/ECN-Phyllis#wheatstraw> (accessed September 29, 2022).
- [53] M.R. Rover, A. Aui, M.M. Wright, R.G. Smith, R.C. Brown, Production and purification of crystallized levoglucosan from pyrolysis of lignocellulosic biomass, *Green Chem.* 21 (2019) 5980–5989, <https://doi.org/10.1039/C9GC02461A>.
- [54] ICIS, Acetic Acid - Price, (2016). <http://www.icis.com/chemicals/acetic-acid/> (accessed September 25, 2022).
- [55] J. Wang, Z. Lu, A. Shah, Techno-economic analysis of levoglucosan production via fast pyrolysis of cotton straw in China, *Biofuels, Bioprod. Biorefining.* 13 (2019) 1085–1097, <https://doi.org/10.1002/bbb.2004>.
- [56] J.F. Peters, Pyrolysis for biofuels or biochar? A thermodynamic, environmental and economic assessment, *Universidad Rey Juan Carlos*, 2015. <https://dialnet.unirioja.es/servlet/tesis?codigo=113788>.
- [57] EC, Electricity price statistics, Eurostat - Stat. Explain. (2016) 1–10. http://ec.europa.eu/eurostat/statistics-explained/index.php/Electricity_price_statistics#Electricity_prices_for_industrial_consumers (accessed September 2, 2022).
- [58] P.L. Cruz, D. Iribarren, J. Dufour, Life cycle costing and eco-efficiency assessment of fuel production by coprocessing biomass in crude oil refineries, *Energies* 12 (2019) 4664, <https://doi.org/10.3390/en12244664>.
- [59] R.K. Sinnott, G. Towler, *Chemical Engineering Design - Principles, Practice and Economics of Plant and Process Design* (2nd Edition), 2013.
- [60] M.M. Wright, D.E. Daugaard, R.C. Brown, J.A. Satrio, Techno-economic analysis of biomass fast pyrolysis to transportation fuels, 2009. <https://www.nrel.gov/docs/fy11osti/46586.pdf>.
- [61] K. Meesters, W. Elbersen, P. van der Hoogt, H. Hristov, Biomass pre-treatment for bioenergy. Case study 5: Leaching as a biomass pre-treatment method for herbaceous biomass. *Sugar Cane Trash and Palm Oil Mill Residues*, 2018.
- [62] I. Itabaiana Junior, M. Avelar do Nascimento, R.O.M.A. de Souza, A. Dufour, R. Wojcieszak, Levoglucosan: a promising platform molecule? *Green Chem.* 22 (18) (2020) 5859–5880, <https://doi.org/10.1039/D0GC01490G>.