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Abstract: A flow-through reactor for the extraction of hemicelluloses with hot pressurized water was scaled up. Experiments were conducted with the two systems using catalpa wood as raw material at different temperatures, to determine the effectiveness of the scale-up.
The one pilot reactor system was subsequently upgraded by designing and building a manifold system capable of working in series. Technological innovations implemented, permitted a continuous operability, minimizing downtime when replacing the biomass during loading and unloading phases.
A study was performed to determine the evolution of the composition and molecular weight of the extracted solution, by varying its residence time within the system. The plant worked homogeneously and there were no deviations in the characteristics of the liquid product flowing from one unit to the next.
The main objective of this work was to verify the possibility of using the plant set-up for an industrial process by comparing two scales.

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Well-respected Editor and Reviewers,

We offer our piece of research to publish in Bioresource Technologies (70.040: Other thermochemical processes).

"Hydrothermal extraction of hemicellulose from lab to pilot scale"

In this research, a pilot multistage flow-through reactor for the liquid hot water extraction of hemicellulose from lignocellulosic biomass was designed, built and tested.

A laboratory-scale plant was initially scaled with a factor of 72 and the effectiveness of the scale-up was verified through experiments with the two systems.

The pilot plant was implemented with technological innovations to become a multistage pilot plant with a continuous operability, minimum downtimes and easiness in the operation.

The evolution of the characteristics of the liquid extract was studied, when changing the liquid and solid residence time within the system, and the operating temperature.

The main fields considered in the paper and the innovation level are:

Process innovative scale-up 

Hydrothermal fractionation 

Process improvement 

We strongly believe that our findings would appeal to the readership of Bioresource Technologies as in this work we propose and test a totally new plant set-up for biomass pretreatment, demonstrating its manageability and speed of operation, key features in an industrial process.

It is the original work of the authors, not previously submitted to BITE. All the authors mutually agree that it should be submitted to BITE.

Sincerely yours,

The authors.

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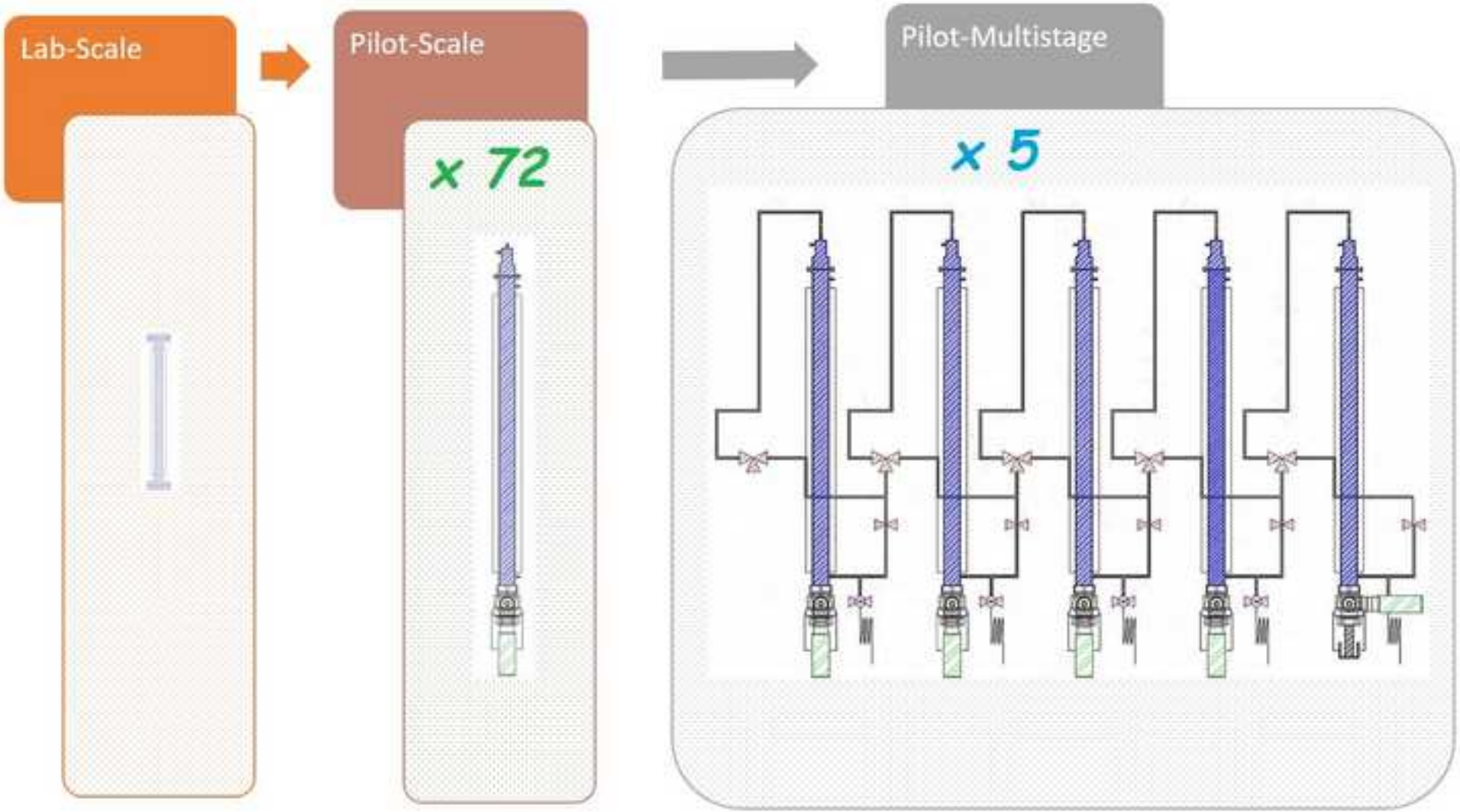

HIGHLIGHTS

- Novel pilot plant for hydrothermal pretreatment of lignocellulosic biomass.
- Optimization of reactor set-up to minimize downtimes in hemicellulose extraction.
- Verification of scale-up efficacy through experiment at different conditions.
- Evolution of the liquid extract when changing its residence time in the system.

Hydrothermal extraction of hemicellulose from lab to pilot scale

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Abstract

A flow-through reactor for the extraction of hemicelluloses with hot pressurized water was scaled up. Experiments were conducted with the two systems using catalpa wood as raw material at different temperatures, to determine the effectiveness of the scale-up.

The one pilot reactor system was subsequently upgraded by designing and building a manifold system capable of working in series. Technological innovations implemented, permitted a continuous operability, minimizing downtime when replacing the biomass during loading and unloading phases.

A study was performed to determine the evolution of the composition and molecular weight of the extracted solution, by varying its residence time within the system. The plant worked homogeneously and there were no deviations in the characteristics of the liquid product flowing from one unit to the next.

The main objective of this work was to verify the possibility of using the plant set-up for an industrial process by comparing two scales.

Keywords

Pilot plant; hemicelluloses; fractionation; biorefinery; hydrothermal.

1. Introduction

Hemicellulose is a biopolymer naturally synthetized by most of the existing trees and plants; its presence in all lignocellulosic biomasses with percentages between 15 and 35% makes hemicellulose the second polysaccharide with the highest abundance in nature after cellulose (Gatenholm et al., 2004). Unlike cellulose, which has technological interest in many fields such as plastic, pharmaceutical and paper industry, hemicellulose applications are being investigated and the interest for this polymer is growing in recent years.

It was demonstrated that hemicellulose polysaccharides have interesting properties in the manufacturing of food additives (Masutake et al., 1994), emulsifiers (Nakamura et al., 2000), plastic film for the protection of foods (Gatenholm et al., 2008) or superabsorbent hydrogels (Zhang et al., 2015). The monomers that constitute hemicellulose are also of great interest. Xylans, present mainly in hardwoods, grasses and straws, are mainly composed by xylose, precursor of high-value products such as xylitol or furfural. Xylitol is produced by hydrolysing xylans and subsequently hydrogenating the xylose monomers. The use of xylitol as a substitute to traditional sugar can help in preventing tooth decay and promote remineralisation of small lesions (Makinen et al., 1995). It can even be of help for osteoporosis prevention (Mattila et al., 2002). Furfural, a dehydration product of xylose, is used as a solvent in petrochemical industry to extract dienes (such as those used to produce synthetic rubber) from other hydrocarbons and it is also an intermediate product in the production of solvents such as furan (Hoydonckx et al., 2000).

Because of its non-crystalline morphology, in contrast to that of cellulose, hemicelluloses are generally broken and degraded during conventional pulping processes. However, thanks to biomass pre-treatments and novel separation processes it is possible to obtain and isolate hemicellulose oligomers with suitable characteristics to fabricate several specialised materials.

Methods for extraction of hemicelluloses

Traditional methods used for the extraction of hemicelluloses from biomass involve the use of mineral acid solvents. For instance, acid hydrolysis with concentrated H_2SO_4 or HCl is an effective way to extract and convert approximately 100 % of cellulose and hemicellulose into monomers. Yet, special equipment resistant to corrosion and a recover of acid after hydrolysis are required under such conditions.

Dilute acid hydrolysis is a wide used method. H_2SO_4 or HCl with concentration in the range of 2-5 % are generally used (pH close to 0), at 160 to 230ºC. This treatment extracts hemicellulose from biomass effectively and hydrolyses it into monomeric sugars and often into degradation product such as furfural or 5-hydroxymethylfurfural (Ur-Rehman et al., 2015). These processes are suitable if the main purpose is to obtain a high yield of monosaccharides. Nonetheless, if the aim is to obtain oligomers of hemicellulose for fabrication of specialised materials such as gel or plastics, other pre-treatments are required.

Hydrothermal treatment is a technique with several advantages over the methods previously mentioned. Depolymerisation of oligomers and degradation of monomers is notably reduced. Furthermore, as the unique solvent employed is water, the environmental impact is reduced. Pressurized water at temperatures above 120 ºC is subjected to an ionization process forming H_3O^+ ions that induce the partial depolymerisation of hemicellulose. Hemicellulose has acetyl groups alternatively embed in its pentose-hexose structure. Cleavage of acetyl groups consequently leads to the further formation of H_3O^+ ions that catalyses the depolymerisation of hemicellulose. This process, called autohydrolysis, fits very well when the main purpose is to obtain hemicellulose oligomers with higher selectivity over monomers formation and monosaccharide degradation (Garrote et al., 1999).

Hydrothermal extraction plants

There is a huge number of examples regarding hydrothermal hydrolysis of biomass at laboratory scale. In most cases, the process is carried out in batch reactors (dos Santos Rocha et al., 2017; Garrote et al.,

2001b; Lu et al., 2017; Sánchez-Bastardo et al., 2017), being a minor number of researches conducted with semi-continuous flow-through reactors (Gallina et al., 2016; Tanaka et al., 2012; Yedro et al., 2015a) or continuous reactors (Cantero et al., 2015; Kazachkin et al., 2014).

Flow-through pre-treatments were recognised to be the best in terms of extraction efficiency and energy economy: thanks to a more effective mass transfer, they allow highest extraction yields respect to batch reactors, and they do not require extreme milling of biomass and suspension pumping such in the case of continuous-flow reactors.

Pilot plants for hydrothermal extraction of hemicellulose are not many. One example is the Integrated Biomass Utilization System (IBUS) which converts biomass into sugars and lignin, and then to ethanol and energy, by using three reactors (Larsen et al., 2008; Petersen et al., 2009; Thomsen et al., 2008). This system uses a particle pump to move the biomass into the high-pressure systems.

In a previous project developed by our research group, a laboratory-scale flow-through reactor was developed, operated and optimised (Gallina et al., 2016; Yedro et al., 2015a; Yedro et al., 2015b). That rig, similarly to most of the existing lab plants, including pilot plant reactors (Kilpeläinen et al., 2014; Reynolds et al., 2015), consisted of a stainless steel tube filled with biomass, axially crossed by a constant flow of pressurized hot water.

One of the main difficulties in this kind of system was to properly load the raw material and discharge the spent solid contained in the reactor once the extraction process was completed. In fact, the wet biomass swells and agglomerates inside this kind of reactors, forming a compact structure difficult to remove without stopping the operation and being necessary to open the reactor.

Sometimes brute force methods, such as drilling, are necessary to extract the compacted-swollen spent solid. In an industrial context, this implies long periods of inactivity and consequently an economic disadvantage. An example can be found in delayed coking, where the coke vessels operate in semi-batch and high pressure water cutting is needed to recover the final coke product (Predel, 2000).

A good technique to solve this problem is to introduce biomass into a cartridge, which can be inserted and removed quickly, as in the system designed by Smirnova et al. (Reynolds et al., 2016; Reynolds et al., 2015; Zetzl et al., 2012).

Results obtained with our laboratory-scale installation, drove our group to design a semi-continuous pilot plant. Initially, a scaled-up reactor was built, with a volume 73 times bigger than our laboratory unit, where biomass could be replaced thanks to the insertion and removal of a cartridge through a ball valve placed on the bottom of the reactor.

The system was then integrated with some characteristics of a batch-wise cascade reactor located in Åbo Akademi (Finland) (Grénman et al., 2011; Rissanen et al., 2014a). That system consisted of 5 Parr units containing biomass, in which a flow of water circulated in closed loop. Each unit could be excluded from the system thanks to a valve system that allowed to deviate the water flow.

After further improvements, we designed a plant consisting of five semi-continuous reactors, each one working in series with the others or with the option of being excluded from the system. A manifold of valves and cartridges, which will be explained later in this work, made possible to extract hemicellulose from biomass without needing to stop the plant. It was even possible to cool down and disassemble the reactors separately during the loading and unloading phases, thus minimizing downtime. The extraction process could be carried out in a pseudo-continuous way, replacing rapidly the raw material and entirely recollecting the spent solid.

In the first part of this paper, we will focus on the scale-up of a laboratory equipment, we will discuss the scale-up criteria and how we verified the efficiency of the scale up.

Subsequently, we will explain how the pilot reactor was implemented to become a multistage flow-through reactor.

The system was then comprehensively tested by a temperature study, analysing the yield of hemicellulose extraction and its molecular weight. This operation allowed to study the variations in the characteristics of extracted hemicelluloses varying the residence time of the liquid product within the system. It was also studied the depolymerisation and degradation of oligosaccharides varying their

residence time inside the plant. The objective of this work was to create a system able to operate in a continuous and fast way, allowing to obtain a product with constant characteristics and composition, and being considered for an industrial production of hemicellulose by hydrothermal extraction.

2. Experimental

2.1 Raw material characterization

Catalpa bignonioides wood used as the main raw material in all the experiments was originated from Valladolid (Spain). This species was chosen for its abundance in the Castilla y Leon area and the easiness to find pruning residues.

Dry wooden branches were grinded with a chipper, obtaining wood chips with variable particle size between 0.6 and 3.5 cm (showed in Supporting Information). They were kept in a dry room inside closed bags until the day of the tests. No bark removal was carried out, since the goal was to start off from low cost biomass, which had undergone a minimum number of pre-treatments.

The composition of the raw material in terms of structural carbohydrates, extractives, ashes, humidity and lignin were determined according to the standard methods published by National Renewable Energy Laboratory (NREL) (Hames et al., 2005; Sluiter et al., 2008a; Sluiter et al., 2008b; Sluiter et al., 2008c). Dried biomass was treated with water in a Soxhlet equipment, in order to remove the water soluble extractives, and lately with ethanol to remove remaining extractives. 300 mg of dried and free-extractives solid were hydrolysed in 3 mL of 72% wt sulphuric acid solution for 60 min at 30 °C. The mixture was diluted using 84 mL of Milli-Q water and heated in autoclave at 120 °C for 60 min. Solid was separated from the liquid solution by vacuum filtration and placed in a muffle at 550 °C for 24 h. The remaining residue was weighted before and after this step to calculate the insoluble lignin and the ash content of the sample. A liquid aliquot was analysed with UV-Vis spectrophotometer at 320 nm with extinction coefficient of 34 $Lg^{-1}cm^{-1}$ (Sun, Cao, Li, Xu, & Sun, 2014) to calculate the amount of soluble lignin. Another liquid aliquot was neutralized to pH range 6 to 7, filtered using a 0.2 µm membrane and analysed by HPLC to determine the carbohydrates composition.

2.2 Analytical methods

2.2.1 Analysis of liquid samples composition

The total number of compounds contained in the liquid samples was determined by hydrolysing oligomers extracted during the process. 0.8 mL of sulphuric acid (72%) and 15 mL of Milli-Q water were added to 5 mL of liquid samples. This solution was autoclaved at 121 °C for 1h. Prior to the HPLC analysis, liquid samples were filtered (Pore size 0.22 m, Diameter 25 mm, Nylon; FILTER-LAB) (Sluiter et al.).

Original liquid samples (before acid hydrolysis) obtained by the extraction process were also filtered and analysed with HPLC.

The column used for the separation of the compounds was SUGAR SH-1011 Shodex at 50.0 ºC with a flow of 0.8 mL/min, using a solution of 0.01N of sulphuric acid and water Milli-Q as mobile phase. A Waters IR detector 2414 and Waters dual λ absorbance detector 2487 (210 nm and 254 nm) was used to identify the sugars and their derivatives.

The calibration reagents used for HPLC analysis were: cellobiose (+98%), glucose (+99%), fructose (+99%), glyceraldehyde (95%), pyruvaldehyde (40%), arabinose (+99%), glycolaldehyde (+98%), 5-hydroxymethylfurfural (99%), lactic acid (85%), formic acid (98%), glucuronic acid (99%), mannose (+99%), xylose (+99%), galactose (+99%), rhamnose (+99%), galacturonic acid (+99%), furfural (+99%), acetic acid (+99%), all of them purchased from Sigma-Aldrich and used without further modification.

For the analysis of sugars, sulphuric acid (96%) and calcium carbonate (+ 99 %), purchased from Panreac were used.

2.2.2 Analysis of molecular weights

Molecular weight of the hemicelluloses in the liquid extract was determined by Size Exclusion Chromatography (HPLC-SEC). The column used was a GPC column (SB-804 HQ; Shodex) protected by a guard column (SB-G; Shodex) at 35 ◦C with a flow rate of the mobile phase (NaNO3 0.1 M +

190 NaN3 0.02% in Milli-Q water) set at 0.5 mL min−1. A Waters IR detector 2414 was used for the
191 determination of the molecular weight of the extracted hemicelluloses. Calibration curve was obtained
192 with a set of eight pullulan standards (STANDARD P-82; Shodex) ranged between 6.1 and 642 kDa of
193 average molecular weight, dissolved in milli-Q water.
194
195 **2.2.3 Determination of pH**
196 The pH of the extracted solution (hydrolysate) was measured online, with intervals of 1 minute in the
197 liquid outlet. An electronic pH-meter (Crison CRI10123.99) was used.
198
199 **2.3 Raw Material Composition**
200 Humidity, determined after drying a sample of wood in a convection oven at 105 ºC, was calculated to
201 be 14% wt. Dry raw material was composed by: 20.8% of extractives, 16.2 % of lignin, 0.3% of ashes,
202 32.3% of cellulose (glucose), 23.7% of hemicelluloses (xylose, arabinose and acetic acid) and 6.8% of
203 pectins (galacturonic acid). Amounts of single compounds are represented in Table S1 in the Supporting
204 Information.

205 Along the manuscript, xylose will be chosen as the monosaccharide representing the hemicelluloses, as
206 xylans constitutes the main hemicelluloses proceeding from hardwoods like *Catalpa bignonioides*
207 (Yoon et al., 2016).
208 Wood proceeding from branches and bark is known to have a great amount of extractives respect to
209 stem wood (Krutul et al., 2014; Nurmi, 1992) and these results were confirmed by our composition
210 analysis.

211 46.3% of extractives was water soluble, while the remaining 53.7% was soluble in ethanol. This
212 proportion is similar to that found from other authors in other species like *Eucalyptus globulus* (Morais
213 & Pereira, 2012).
214 12.9% of the water soluble extractives were monosaccharides and sugar acids (32.0% glucuronic acid,

28.0% glucose, 14.0% xylose and 26.0% arabinose).

2.4. Experimental set-up and operation

This section is explained later within section 3 (lab and pilot scale for 1 reactor) and section 4 (dedicated to the pilot 5-reactor system manifold), as the scale-up was one of the objectives of the work.

3. Reactors scale-up: from lab scale to pilot scale

The set-up and the operational tips of both the laboratory scale and pilot scale reactors are described in this section; the criteria for the scale up is explained in detail. A discussion on the characterization of the hydrolysate effluents produced with these systems is included at the end of the section, comparing the results and assessing the effectiveness of the scale-up.

3.1 Laboratory scale flow-through reactor

Laboratory-scale reactor is schematized in Figure 1. A PU-2080 HPLC pump (P-01) took water from a deposit (D-01) and propelled it through a concentric tube heat exchanger working in counter-current mode (E-01, 2m length, 1/8”-1/4”). Then water passed through a pre-heater (H-01, 200 cm of 1/8” SS 316 pipe, electrically heated by two electric resistors of 300 W) which ensured a uniform temperature at the reactor inlet. Water entered from the top of the reactor (R-01), consisting of a SS316 pipe (R-01, 38 cm length, ½” O.D., 0.38” I.D.), charged with wood chips. Reactor was covered on the top and on the bottom by two metallic filters, in order to avoid the loss of solid particles during the experiments. The reactor was heated by three electric clamp resistors of 300 W/each, placed axially along a machined aluminum bar with 5.08 cm O.D. Outlet flow passed through a concentric tube heat exchanger E-01 (preheating the inner flow).

Pressure was controlled by a Go-back pressure valve (BPV-01) installed at the liquid outlet. The outer flow pH was measured online using an electronic pH-meter (Crison PH 29).

3.1.1 Operation of laboratory reactor

Wood from *Catalpa bignonioides* was used as raw material; 6 g of chips with a medium particle size of about 0.6 cm were loaded in the reactor R-01. A cold liquid pressure test was made before each experiment: cold water was circulated through the system for 5 min in order to check the presence of leaks and to ensure the wetting of the wood. After that, the pump was switched off, while electric heater and clamp resistances placed along the reactor were set at a temperature of 20 ºC above the operating temperature. When the temperature was reached, water was pumped through the system, starting the experiment (time 0). Experiments carried out with other raw materials in the laboratory scale reactor (Gallina et al., 2016), indicated that the optimal flow to get a good mass transfer with the minimum amount of water, corresponded to 3.5 mL/min; the same flow rate was used in this work.

The first sample (time 0) was collected as soon as the first drop of liquid came out from the system. Water reached the operating temperature in about 7 min from the taking of the first sample. Samples were collected after 5, 10, 20, 30, 40, 60 and 90 minutes from the beginning of the operation. At the end of the process, the heating was turned off and fresh water was passed through the system to cool down the reactor. When a temperature of 50 ºC was reached, the pump was switched off, the system was depressurized and water was let to flow out. The reactor was finally dismounted, placed in a mechanical grip and, using a steel punch and a hammer, the wet solid was removed.

3.2 Scale-up to single stage pilot reactor

The scale-up of the laboratory reactor was made by following the criteria indicated in Table 1. The volume of the pilot reactor was 2000 mL, 73 times bigger than the laboratory-scale reactor. Geometrical similarity between the two systems was maintained, by keeping constant the ratio between length and internal diameter (L/ID). An optimal flowrate of 250 mL/min was set in the pilot system to have the same superficial velocity of water as in the lab-system. The porosity of the bed was also preserved in both reactors, to have the same residence time of the liquid (aprox. 6.0 min).

One of the objectives of this work was to minimize the difficulties of replacing the biomass in the extractor in order to ease the operation and maintenance of the pilot reactor. At laboratory scale, there are many methods that can be used to remove the spent solid (some of them are 'brute-force' methods, e.g. drilling, pushing out with compressed air, etc.) that are difficult to use at pilot or industrial systems. To facilitate the replacement of biomass in the flow-through reactor, a cartridge mode has been implemented.

The reactor unit consisted of 3 main parts (Figure 2a):

- An open cylinder, constructed with a wire mesh (7) that could be opened longitudinally. Internal diameter of the cylinder was 4 cm and length was 159 cm.
- Two stainless steel cylinders with the same diameter (4 and 5), one of which (5) had several orifices (with a diameter of 1 mm) at the bottom (6), working as a filter. A glass wool layer could be placed over the holes to decrease the dimension of the voids.

  The wire mesh was inserted between the two cylinders, forming a cartridge, which was filled with biomass. The inner diameter of the two cylinders was 4.3 cm; so that the mesh adhered perfectly to the walls. The cylinders thickness was 2 mm.
- An outer stainless-steel cylinder (2) with two opening (A and B) closed at the upper end with a mechanized flange (1) with an opening (C), and with a ball valve (3) screwed on the lower end. Internal diameter of the valve and of the cylinder was 5.1 cm, so that the cartridge could be introduced from the bottom and inserted completely into the system.

This system greatly facilitated the replacement of biomass, which could be removed from the system by simply opening the valve and pulling out the cartridge. The longitudinal opening of the wire mesh, moreover, reduced the effort required to remove the wet biomass from the cartridge.

A flow diagram of the single-stage pilot system is represented in Figure 2b. A constant flow of water was drawn from a vessel (D-01) and propelled with a Tuthill DGS.68 pump (P-01) through the external tubes of a system composed by three concentric tube heat exchangers E-01 to E-03 (18 m total length,

1/4” internal tube-3/8” external tube) and then through an electric heater H-01 with a maximum power of 5 kW.

Given the high power of the heater, a special procedure was designed to avoid the overheating of this unit. Unlike in the laboratory scale system, where the heater was left over for a time heating with no contact with water, in the case of the pilot plant, water flowing through a coil was in constant contact with the heater wall.

A three way valve (3V-01) was placed between the heater and the reactor, which could direct the liquid flow to the inlet of the reactor (placed on the top) or out of the system. A ball valve (V-01) was placed just after the outlet of the reactor.

During the preheating phase, the 3-way valve was turned so that water did not enter the reactor, while valve V-01 was closed to prevent water from returning in the reactor through its output.

Water stream entered subsequently in the inner part of the concentric tube heat exchangers (E-01 to E-03), where it was cooled down by the feeding water flowing countercurrent in the external part, before leaving the system through a Go-back pressure valve (BPV-01). In this way it was possible to pre-heat the water to the desired temperature before introducing it into the reactor.

Reactor R-01 was homogeneously coated with four clamp resistors, which power was 250 W/each (total nominal power was 1 kW).

The entire system was thermally insulated with a layer of 2 cm glass wool, protected with aluminum foil.

Temperature of water entering and leaving the reactor was measured with two thermocouples placed at the inlet and at the outlet of R-01.

A flow-meter was placed after the pump to measure the liquid flow rate. An online pH-meter was placed after the Go-back pressure valve to measure the pH of the solution produced by the process.

3.2.1 Operation of single stage pilot reactor

The cartridge was assembled by introducing the wire mesh between the two half cylinders then. 250 g of chips with a medium particle size of about 2.0 cm were placed inside. The quantity and size of the particles was selected to maintain the same porosity as in the laboratory system.

At the beginning of the operation, the cartridge was introduced into the reactor through the bottom, and the ball valve (3) was closed.

A flow of cold water was pumped inside the reactor from the top, until it was completely filled. During this procedure, ball valve V-01 was closed to keep the water inside the reactor.

Another ball valve (V-02), was connected to an outlet (B) of the reactor placed on the top. This valve was opened during the filling procedure, and was connected to a plastic container (C-01). When water wet the container the reactor could be considered completely filled. At this moment, the ball valve V-02 was closed and the valve (V-01) was opened, letting water exiting from the reactor.

A cold liquid pressure test was made, by increasing the pressure of the system to 17 bar. Subsequently, the three-way valve was switched and the valve (V-01), so that the flow of water by-passed the reactor.

Heater was turned on to heat-up the liquid flow 20 ºC above the operating temperature; water contained in the reactor was preheated to 95 ºC through the clamp resistances which wrapped it around. Temperature of water inside the reactor was set to a value minor than 100 ºC to avoid the extraction of structural carbohydrates.

When the water reached the desired temperature, the three-way valve was switched, and the flow was directed into the reactor; at the same time, the ball valve (V-01) was opened, letting water exiting the reactor.

Time 0 (zero) was set at this moment and sample 0 (zero) was collected from the system outlet. Other samples were collected after 5, 10, 20, 30, 40, 60 and 90 minutes from the starting of the operation.

344 At the end of the process, the heating system was turned off and fresh water was passed through the
345 system to cool it down. When a temperature of 50 ºC was reached, the pump was switched off, the
346 system was depressurized and water was let to flow out. The ball valve (3) on the bottom of the reactor
347 was opened and the cartridge containing biomass was extracted and dismounted to remove the solid.
348
349 **3.3 Comparison between results obtained with laboratory and pilot reactor**
350 Hydrothermal extraction was carried out with the laboratory scale and with the pilot reactor at 160 and
351 170 ºC. Figure 3a represents the cumulative yields of total xylose, produced with the two systems after
352 the extraction process and the acid hydrolysis of the solution obtained. Yield was calculated as the ratio
353 between the total mass of the xylose extracted and the total mass of xylose in the wood contained in the
354 reactor at the beginning of the experiments.

355 A cumulated yield of 33.9% was obtained after 90 minutes of operation, using the laboratory scale
356 reactor at 160 ºC; a yield of 35.7% was reached with the pilot reactor at the same temperature and
357 extraction time.

358 In experiments conducted at 170 ºC, the yields increased in both cases, reaching final values of 38.8%
359 and 41.7% when using the lab-scale and the pilot reactors respectively. Yields of all the compounds
360 extracted are represented in Table S2 in the Supporting Information.

361 The positive effect of temperature in increasing the extraction yield is well known and widely
362 documented (Nitsos et al., 2016; Qian et al., 2015; Yedro et al., 2017). However, in this work, the main
363 concern was to identify the differences that occurred when the process was scaled-up.

364 Figure 3b shows the percent deviation between the yields obtained with laboratory scale and pilot scale
365 reactors, at 160 and 170 ºC.

366 At both temperatures, the deviations followed a decreasing trend: it was 100% at time 0, after 5 min it
367 decreased to 64.0 % in the experiment at 170 ºC and 44.0 % at 160 ºC. After 20 min the deviations
368 reached negative values and then tended to 0.

369 The "100% deviation", found at time 0 was associated to the fact that while with the laboratory system
370 no xylose was produced, small amounts were detected in the solutions proceeding from the pilot plant at
371 the very beginning of the extraction. The presence of this monosaccharide, rather than to hemicelluloses
372 breakdown, was almost certainly due to the free sugars contained in the biomass, which can be extracted
373 at temperatures below 100 ºC (Alañón et al., 2009). Considering the composition of water soluble
374 extractives, determined as explained in the section 2.3, it was calculated that xylose extracted at time 0
375 with the pilot reactor, corresponded to the 25.8% of the monomeric xylose in the raw material. This
376 initial yield of monomeric xylose is the same in the experiments carried out at 160 and 170 ºC, as
377 temperature of water inside the reaction chambers was always set at 95 ºC (as explained in section 3.2.1)
378 at the beginning of the operations.

379 The deviations between the yields obtained with pilot scale and laboratory scale plants were higher
380 during the first 10 minutes of extraction. This behaviour could be due to: (1) the different temperature
381 profile followed during the process, as represented in the Supporting Information and (2) the differences
382 in the time scale due to the piping, which length change have more influence at the beginning of the
383 process, when the slope in the extraction curve is high.

384 The warming up to the operating temperature occurred faster in the pilot plant (3 minutes less) in
385 comparison with the laboratory scale system. This delay, due to the different method employed in the
386 heating, is responsible for the initial deviation between the yields obtained in the two systems. In the
387 pilot plant, the wood particles were completely submerged in water before starting the process. Then,
388 they had undergone to a preheating to 95 ºC, during which their structure weakened and released part of
389 the water-soluble compounds.

On the other hand, in the laboratory scale plant, part of the water that was injected during the pressure control step left the system during the preheating phase, when the pump was switched off. Thus, chips impregnation was less effective than in the pilot reactor, leading to a less breakdown of the wood particles (Bäckström et al., 2016; Malkov et al., 2001). The lower amount of water inside the reactor also resulted in a greater inertia to reach the operating temperature, as it took about 5 min to completely fill the system and then warm it up.

Figure 3c represents the cumulative yield of monomeric xylose obtained at different times of extraction in the pilot and laboratory scale plant. As it is known, temperature favours the extraction of hemicellulose oligomers and increases hydrolysis and formation of monosaccharides (Rogalinski et al., 2008), which is in according with the results shown in Figure 3c. An increasing in temperature from 160 to 170 ºC meant an increasing in the yield of around 2%.

Comparing subplots in Figure 3 it is possible to deduce that the yield was slightly higher in the pilot reactor than in the lab scale in general. The higher differences appeared during the first 20 minutes of extraction, attributable mainly to the different preheating procedure. No degradation product, such as furfural (from xylose cyclodehydration) or 5-hydroxymethylfurfural (5-HMF from glucose dehydration), were detected in the experiments, suggesting that the temperatures and residence times tested were not strong enough to decompose the monosaccharides.

4. Multistage pilot flow-through reactor

After establishing the effectiveness of the scale-up, several modifications were made in the pilot plant, aimed at conducting the hydrothermal extraction in a continuous and rapid way: the single stage flow-through pilot plant was implemented to become a multistage flow-through pilot plant.

This section will explain the setup of the manifold-system and the standard operating mode for which it was designed. Finally, a study was conducted to verify the possibility of a continuous production of hemicellulose.

4.1 Set-up of multistage reactor

The complete layout of the plant is shown in Figure 4. Five reactors with the same geometry and operating principle as the one shown in Figure 2a, were connected in series (R-01 to R-05). A three-way valve (3V-01 to 3V-05) was placed before each reactor (manifold). Each valve could divert the flow to the reactor inlet or to the next 3-way valve, by-passing the reactor. Ball valves (V-01, V-03, V-05, V-07 and V-09) placed after the reactors could be closed to prevent water return.

Right after the outlet of each reactor, needle valves (NV-01 to NV-05) connected to concentric tube heat exchangers (ES-01 to ES-05) allowed for the withdrawn of liquid samples from the reactors. Liquid solutions flowed through the internal pipe of heat exchangers (1 m length, 1/8" internal tube- 1/4" external tube) when needle valves were open, and were cool-down by tap water flowing through the external pipe.

A centrifugal pump Marathon Electric 5KH36 (P-02) took fresh water from a vessel (V-02) and transferred it through a pipe, ball valves (V-11 to V-15) could be opened to let water enter into the reactors. Valves V-02, V-04, V-06, V-08 and V-10, connected to plastic containers (C-01 to C-05) worked as level control system: reactors were filled when first drops wetted the containers.

Pump P-01 (Tuthill DGS.68) transferred water from a vessel (D-01), to the external section of three concentric tube heat exchangers E-01 to E-03 (18 m total length, 1/4" internal tube-3/8" external tube) and then through an electric heater H-01 with a maximum power of 5 kW.

Each reactor was coated with four clamp resistors with a total power of 1 kW/reactor. The water left the system after being cooled down in heat exchangers E-01 to E-03, and depressurized through a Go back-pressure valve (BPV-01). A pH meter placed after the valve measured online the pH of the final solution every minute. The whole system was thermally insulated with a layer of glass wool (about 2 cm) covered with aluminum foil.

4.2 Standard operation of multistage reactor

441 In a standard operation, three reactors (R-01, R-02 and R-03) were charged with biomass by inserting
442 the cartridge, as explained in section 3.2.
443 *System preparation*
444 Valves (V-01, V-03, and V-05) placed after the outlet of the reactors were closed.
445 Centrifugal pump P-02 was turned on, valves V-11, V-12, and V-13 were opened to let water enter into
446 the reactors (dotted arrows), and valves V-02, V-04 and V-06 were also opened to let water flow-out to
447 plastic containers (C-01 to C-03) when reactors were completely filled.
448 When reactors were filled, the pump P-02 was switched off, while valves V-11, V-12, V-13 and V-02,
449 V-04, V-06 were closed.
450 At this time, pump P-01 was turned on and set to the desired flow rate, feeding the system with fresh
451 water.
452 3-way valves 3V-01, 3V-02 and 3V-03 were set in order to let water enter into the reactors, valves V-
453 01, V-03, and V-05 were opened to let water flow out.
454 The direction of the flow is represented by the continuous arrows in Figure 4: water flowed through the
455 external pipes of heat exchangers (E-01 to E-03), through the spirally wound pipes around the heater H-
456 01, entered reactor R-01 from the top and left it from the bottom, passing through the biomass
457 contained.
458 3-way valve 3V-02 and 3V-03 connected reactors R-02 and R-03 in series with R-01.
459 Water by-passed reactors R-04 and R-05, entered into the internal pipes of heat exchangers (E-01 to E-
460 03) and left the system.
461 *Pressurization and warming up*
462 Pressure of the system was increased to 17 bar and a cold liquid pressure test was made, stabilizing at
463 the same time the liquid old-up of the system.
464 When the liquid flow-rate (measured through a flow-meter placed after pump P-01) was constant, 3-way
465 valves (3V-01 to 3V-03) were switched to make water by-pass the reactors R-01 to R-03, while valves
466 V-01, V-03 and V-05 were closed to avoid water return.

Circulating water flow was pre-heated to 20 ºC above the operating temperature (by turning on the heater H-01), while water contained in reactors R-01 to R-03 was heated to 95 ºC by turning on the clamp resistors which covered the reactors.

Extraction

After reaching the desired temperature, 3-way valves 3V-01 to 3V-03 were switched and hot water flowed through the three reactors, extracting soluble compounds from biomass.

Liquid samples could be withdrawn from each reactor at regular times, by opening the needle valves (NV-01 to NV-03).

When it was desired to interrupt the extraction in one of the reactors, i.e. R-01, the unit was isolated from the system, by switching the 3-way valve that preceded it (3V-01) and closing the ball valve V-01 simultaneously. Needle valve (NV-01) was opened to remove the water contained in the reactor and to depressurize it. Ball valve on the bottom of the reactor was opened and the cartridge containing the biomass was discharged.

Meanwhile, a new cartridge could be loaded in another reactor (i.e. R-04), which was filled with fresh water through pump P-02 and warmed up to 95 ºC. When extraction process ended in reactor R-01, circulating solution was let to enter in reactor R-04, by switching the 3-way valve 3V-04 and extracting compounds from the new biomass.

This operation could be repeated for each unit in the system, in this way each reactor could be integrated into the extraction process or could be by-passed. The system allowed continuous operation: each time that a reactor was stopped to replace the feedstock, another reactor could operate. Removal of the raw material was easy and fast, and it could be done without the necessity of disassembling the extraction unit. Moreover, all the solid could be recollected at the end of the extraction.

4.3 Extraction in series in the multistage pilot reactor

To assess the ability of the plant to work in a continuous way, with the possibility to quickly replace the biomass, as described in the paragraph 4.2, it was necessary to verify that the reactors worked in a

493 homogeneous manner and that there were no alterations in the composition of the effluent produced by
494 the individual reactors.
495 Another important matter to study was the evolution in the composition of the extracted products,
496 varying their residence time within the system, to understand if there was degradation or
497 depolymerization of the hemicelluloses extracted when flowing from one unit to the other.
498 Experiments were carried out at four different temperatures (140, 150, 160 and 170 ºC), using three
499 reactors connected in series, with a constant water flow of 15 L/h. Temperature profiles inside the
500 reactors are depicted in the Supporting Information. The temperature of the water flow over time is
501 plotted (see SI): before the heater (after preheating in the heat exchangers), after the heater (before
502 reactor R1), after the reactors (before cooling through the heat exchangers) and at the system outlet
503 (after cooling). In the system, 78% of the heat was recovered in the pre-heating, while 100% of the heat
504 was dissipated during cooling.
505 The reactors were loaded with their respective cartridges, each one filled with 250 g of catalpa wood-
506 chips with an average particle size of 2 cm. Reactors R1 to R3 were then pre-filled with distilled water
507 and pre-heated to 95 ºC.
508 A water stream was also preheated to about 20 ºC above the operating temperature (thus 160, 170, 180
509 and 190ºC) and, at time 0, it was injected inside the first reactor; which outlet flow was entering into the
510 second unit, connected in turn with the third unit in series.
511 In about 3 minutes, the three reactors reached the same operating temperature with a constant water
512 stream flowing through them and preheating the feeding water before exiting the system.
513 The whole operation lasted 90 minutes. Liquid samples were collected at regular intervals of time (0, 5,
514 10, 20, 30, 40, 60 and 90 minutes) from each of the three reactors. After 90 min, the three units were
515 isolated from the system. Then, they were emptied and the cartridges containing the biomass were
516 removed. Pretreated wood proceeding from each unit was entirely collected, dried in an oven at 105 °C
517 and finally weighted. No replacement of biomass was made (although the system is ready for a pseudo-
518 continuous operation).

519 The whole liquid extract proceeding from each experiment was collected in a tank; six vials were filled
520 with 2 mL of every solution and lyophilized to determine the average concentration of all the
521 compounds extracted; the difference between this value and the concentration of hemicellulose in the
522 final solution allowed to calculate the amount of lignin and extractives also resulting from the process.
523 Liquid samples withdrawn from each unit at various residence times were analyzed to determine the
524 composition, the molecular weight and the ratio between monomers and oligomers contained in the
525 products.
526 The mass balance was verified by adding the weight of the processed wood remaining at the end of the
527 experiments and the mass of the total solid extracted during the experiments. The mass of the total solid
528 extracted was calculated as the concentration of solid in the final solution multiplied by the total volume
529 of liquid leaving the system during the experiments.
530

531 **4.3.1 Temperature study in multistage pilot reactor**

532 Figure 5a shows the cumulative yields of total xylose obtained in the multistage pilot plant at four
533 different operating temperatures. Table S3 in the Supporting Information shows the results for all the
534 compounds.

535 The residence time of liquid in the system was 6 min after crossing the unit R1, 12 min after R2, and 18
536 min after crossing R3.

537

538 **4.3.1.1 Yields of extracted hemicelluloses**

539 Yields were calculated as the ratios between the mass of total xylose detected after acid hydrolysis of
540 the liquid samples collected from each reactor and the total xylose contained in the biomass processed
541 respectively in R1, R2 and R3. Figure 5a shows that, as expected, the highest temperatures leaded to the
542 highest yields. Furthermore, the reaction rates increased, since temperature influenced the mass transfer

543 by increasing the diffusion coefficient inside the wood particles and opening the pore structure
544 (Rissanen et al., 2014a).

545 In addition, at constant temperature, the yields were very similar and the variation was minimal at
546 increasing the liquid residence time in the system, as the values were very similar in the samples
547 obtained from the three reactors.

548 Average values of cumulative yield after 90 min of operation were: 9.3±0.7%, 22.0 ±0.5%, 35.1±1.6%
549 and 40.6±1.4%, respectively, at 140, 150, 160 and 170 ºC. The values indicate the average yields and
550 the standard deviations between R1, R2 and R3. Thus, the experimental error was very low (between
551 2.2 and 7.9%).

552 During the process, the extracted products accumulated in the effluent flowing from one reactor to the
553 nextr. The system operated as a long reactor divided into three equivalent sections where the extraction
554 took place homogeneously. Moreover, there was no perturbation in the composition of the liquid
555 effluent flowing from one unit to another.

556 **4.3.1.2 Molecular weight of extracted hemicelluloses**

557 Since the aim of this work was to verify the possibility of using the plant set-up for an industrial
558 process, it was necessary to check if the effluent was homogeneous not only in terms of product yield,
559 but also in terms of composition and length of the oligomers.

560 The molecular weight of the outputs from the three units during the process at different extractions
561 times was then analysed. Values obtained at different temperatures from units R1, R2 and R3, are
562 depicted in figure 5b. Results are represented in Table S4 in the Supporting Information. In all cases, the
563 molecular weight exhibited an upward trend during the first 10 minutes of extraction, and then it
564 remained constant or decreased with the extraction time. An exception occurred in the experiment

565 carried out at 140 °C, wherein the higher molecular weights were obtained after 30 minutes of
566 extraction.

567 In general, the molecular weight decreased with an increasing in the operating temperature. After 90
568 minutes of extraction, the molecular weight of hemicellulose oligomers extracted presented values of
569 4078±23, 2963±142, 1922±95 and 1417±41 Da at 140, 150, 160 and 170 ºC, respectively. Experimental
570 errors were between 0.6 and 5.0%. This behavior was consistent with the results of other authors who
571 worked with other tree species (Rissanen et al., 2014b; Yedro et al.). An increase in temperature is
572 responsible for a higher cleavage of the hemicelluloses, thus reducing the size of the oligomers that
573 detach from the matrix.

574 A similar consideration can be made also by observing the polydispersity index (Mw/Mn) shown in the
575 Supporting Information, which decreased when increasing the temperature.

576 Hemicelluloses break more intensely and faster at high temperatures, for this reason, smaller and more
577 homogeneous molecules were solubilized in experiments at 160 and 170 °C.

578 In the experiment conducted at 140 °C, polydispersity index increased from 1.2-1.7 during the first part
579 of the reaction, reaching a maximum value of 2.5-3.2 after around 30-40 minutes, and then decreasing
580 down to 2.2-2.4 till the end of the experiment. It seems that the extraction started with removing small
581 molecules; as reaction time increased, larger molecules were broken, until their molecular weight was
582 small enough to make them soluble.

583 **4.3.1.2 Acidity of extracted hemicelluloses**

584 As explained so far, the rupture and hydrolysis of the hemicelluloses occurred initially inside the wood
585 chips, because of the kinetics enhanced temperature and catalyzed by the acetyl groups integrated the
586 matrix. Subsequently, the oligomers solubilized in the liquid phase, experience a further hydrolysis
587 catalyzed by the dissolved acetyl groups in the bulk liquid. Higher temperatures favored a greater

588 release and solubilization of acetyl groups, and hence, a stronger and faster hydrolysis of hemicellulose
589 oligomers. Figure 5c shows the instantaneous yield of acetic acid produced in the system during the
590 experiments at different temperatures. The amount of acetic acid increased along with temperature,
591 enhancing the hydrolysis of the oligomers in the liquid phase. Moreover, while the formation of acetic
592 acid at 140 and 150 ° C was almost linear over time, at 160 and 170 ° C there was a maximum
593 production within 5 to 20 minutes from the beginning of the process. Therefore, the molecular weight of
594 the extracted oligomers decreased from the first minutes of reaction at highest temperatures.

595 The variation of acetic acid extracted is reflected also in the pH of the solution leaving the reactor,
596 measured online every minute. Values of pH are depicted in the Supporting Information; more acidic
597 solutions were obtained when increasing the operating temperature. At 140 and 150 ºC, pH decreased
598 during the whole reaction, while at 160 and 170 ºC it reached a minimum value at around 20 minutes
599 and then increased slowly.

600 At constant temperature, the molecular weights of the hydrolysate solutions extracted from the three
601 units had similar values over time. This behaviour can suggest two hypotheses: 1) oligosaccharides
602 extracted from biomass contained in a unit are further hydrolysed in the next unit, in which extraction of
603 new oligosaccharides restored the average molecular weight value, 2) there was a simple accumulation
604 of oligosaccharides and monosaccharides between one unit and the next one, and the oligosaccharides
605 were not subsequently hydrolysed (when their residence time in the system increased passing through
606 the next unit).

607 To solve this question, the ratio between the monomeric xylose extracted during the process and the
608 total extracted xylose in each unit was analysed. In this way, it was possible to determine whether the
609 extracted oligomers were hydrolysed when flowing from one unit to the next one, as shown next.

610

611 **4.3.1.3 Monomers content in the liquid product**

612 Figure 5d shows that the ratio between monomeric xylose and total xylose increased slightly with the
613 residence time of the liquid within the system, with an increasing slope when temperature increased.
614 Values are referred to the cumulative amount of sugars extracted from each unit at the end of the
615 experiments (after 90 min of operation). The highest difference between the maximum and the
616 minimum value resulted at 170 ºC, where the ratio of monomeric xylose to total xylose was 0.18 after 6
617 min and 0.21 after 18 min of liquid residence time. Considering the average values of the ratios at the
618 various temperatures, it can be seen that between 140 and 160 ºC, the values were very similar.
619 However, at 170 ºC, there was a general increasing in monomeric xylose compared to the total xylose
620 extracted. Other authors have found only a slight formation of monomeric xylose from xylans
621 hydrolysis at temperatures lower than 190 ºC and residence time below 20 minutes (Garrote et al.,
622 2001a; Liu & Wyman, 2004; Lloyd & Wyman, 2003). The phenomena may be due to the temperature
623 itself, the main responsible of the cleavage of hemicelluloses, and to the presence of acetic acid, which
624 at temperatures above 160 ºC increased its concentration in the aqueous medium catalysing the
625 breakdown of the solubilized oligomers.

626 Degradation products as furfural or 5-HMF were under the detection limit at the conditions used in these
627 experiments. Therefore, it can be stated that there was an accumulation of the compounds extracted
628 from one unit to the next, while a weak hydrolysis of the oligosaccharides occurred with increasing the
629 liquid residence time, more accentuated at high temperatures.

630 The final mass balance of the four experiments is shown in Figure 6. The errors (the highest error was
631 below 10.5%) which is in the order of other authors in the field. As the temperature rose, an increasing
632 in the solubilized material was noticed, both of the hemicelluloses and of the other compounds, mostly
633 made up of lignin and extractives.

634 The raw material had no ideal characteristics for extracting hemicellulose in a laboratory-level study, as
635 the extractives and lignin content was high and the particle size was large; however, the material could
636 be well used in an industrial context where only a minimal number of treatments is necessary, in order

637 to reduce the costs. The disadvantages represented by this choice are reflected in the low purity of the
638 extract of hemicellulose due to the considerable amount of extractives in the raw material, and in a
639 lower yield respect to other experiments in which the wood particles were smaller and diffusion
640 limitations played a minor role (Kilpeläinen et al., 2014; Rissanen et al., 2014a). A possible solution to
641 improve the process without excessively increasing the operational expenditure (OPEX) could be to
642 perform a first hydrothermal pre-treatment at a temperature between 120 and 140 ºC, during which part
643 of the undesirable soluble compounds would be eliminated without extracting the hemicellulose. Post-
644 treatments to concentrate and fractionate the hydrolysate would be also necessary. Although some
645 improvements are needed in the operations, to obtain products more pure in hemicellulose, the plant
646 described in this document has proved to be versatile and suitable for its intended purpose and can be
647 considered in industrial technology.
648

649 **4. Conclusions**

650 In this work, we have established the basic criteria for the scale-up of a process from a 27.5 mL lab
651 extractor to a 2000 mL pilot extractor for extraction of hemicellulose from biomass with hot pressurized
652 water.
653 A shape parameter of L/D=40, with a bed porosity of 0.71 and a liquid residence time of 6.0 min are
654 efficient for such purpose.
655 From the results obtained, we constructed a manifold of 5-reactors that can operate in series. It was
656 verified that the reactors can work continuously, without changings in the composition of the product.
657

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798

799 **List of Tables**

800 **Table 1.** Scale up criteria from lab-scale to pilot-scale reactor.

801

802 **List of Figures**

Figure 1. Schematic flow diagram of the lab-scale experimental system. Equipment: D-01 water deposit, P-01 pump, E-01 concentric tube heat exchanger, H-01 electric heater, R-01 flow-through reactor, BPV-01 Go-back pressure valve.

Figure 2. a) Section of reactor composition: 1. Cap of the outer SS cylinder; A,B,C. Openings; 2. External SS cylinder; 3. Ball valve; 4. Superior internal cylinder; 5. Inferior internal cylinder; 6. Bottom with orifices of the inferior cylinder, 7. Metallic mesh. b) Schematic flow diagram of the pilot-scale experimental system. Equipment: D-01 water deposit, P-01 centrifugal pump, E-01, E-02, E-03 concentric tube heat exchangers, H-01 electric heater, R-01 flow-through reactor, 3V-01 three way valve, V-01, V-02 ball valves; BPV-01 Go-backpressure valve, C-01 plastic container.

Figure 3. a) Yield of xylose extracted at 160 and 170 ºC with a lab-scale and a pilot-scale reactor; b) Percentage error between yields of xylose obtained with lab-scale and pilot-scale reactor at 160 ºC and 170 ºC. c) Cumulative yields of xylose monomers extracted with a lab-scale and a pilot-scale reactor at 160 and 170 ºC.

Figure 4. Schematic flow diagram of the multistage pilot flow-through reactor where three units are operating in series. Equipment: D-X water deposits, P-X pumps, E-X concentric tube heat exchanger, ES-X concentric tube heat exchangers for sample withdrawn, H-X electric heaters, R-X flow-through reactors, 3V-X three way valves, BPV-X Go-back pressure valves, V-X ball valves, NV-X needle valves, C-X plastic containers. Liquid flow entering in reactors R-01, R-02 and R-03 connected in series and by-passing reactors R-04 and R-05.

Figure 5. a) Cumulative yield of total xylose extracted, obtained from units 1, 2 and 3 during 90 min of operation. b) Molecular weight of hemicelluloses extracted obtained from units 1, 2 and 3 of the system during 90 min of operation. c) Instantaneous values of acetic acid yield obtained from unit 3 of the system during 90 min of operation. d) Ratio between monomeric xylose obtained after the hydrothermal

826 treatment and total xylose extracted after 90 min of operation, as a function of the residence time of the
827 extracted solutions within the system.

828 **Figure 6.** Mass balance calculated at the end of extractions at 140, 150, 150, 160 and 170 ºC.

829 **Table 1.**

830

Parameter	Unit	LAB SCALE	PILOT SCALE
Flow rate	mL/min	3.5	250
Internal diameter	cm	0.96	4
Length	cm	38	159
Volume	cm^3	27.5	2000
L/ID		40	40
Liquid Residence time	min	6.0	6.0
Porosity		0.71	0.71

831 **Figure 1.**

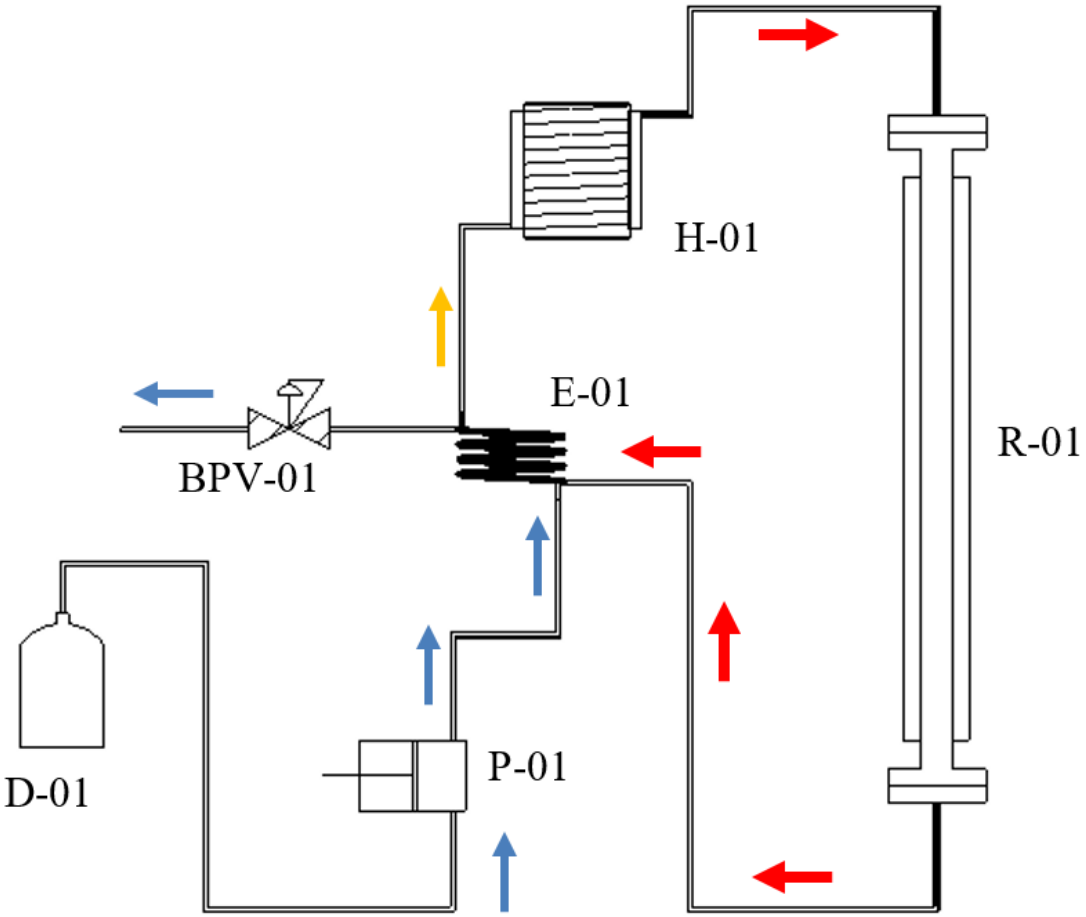

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Figure 2.

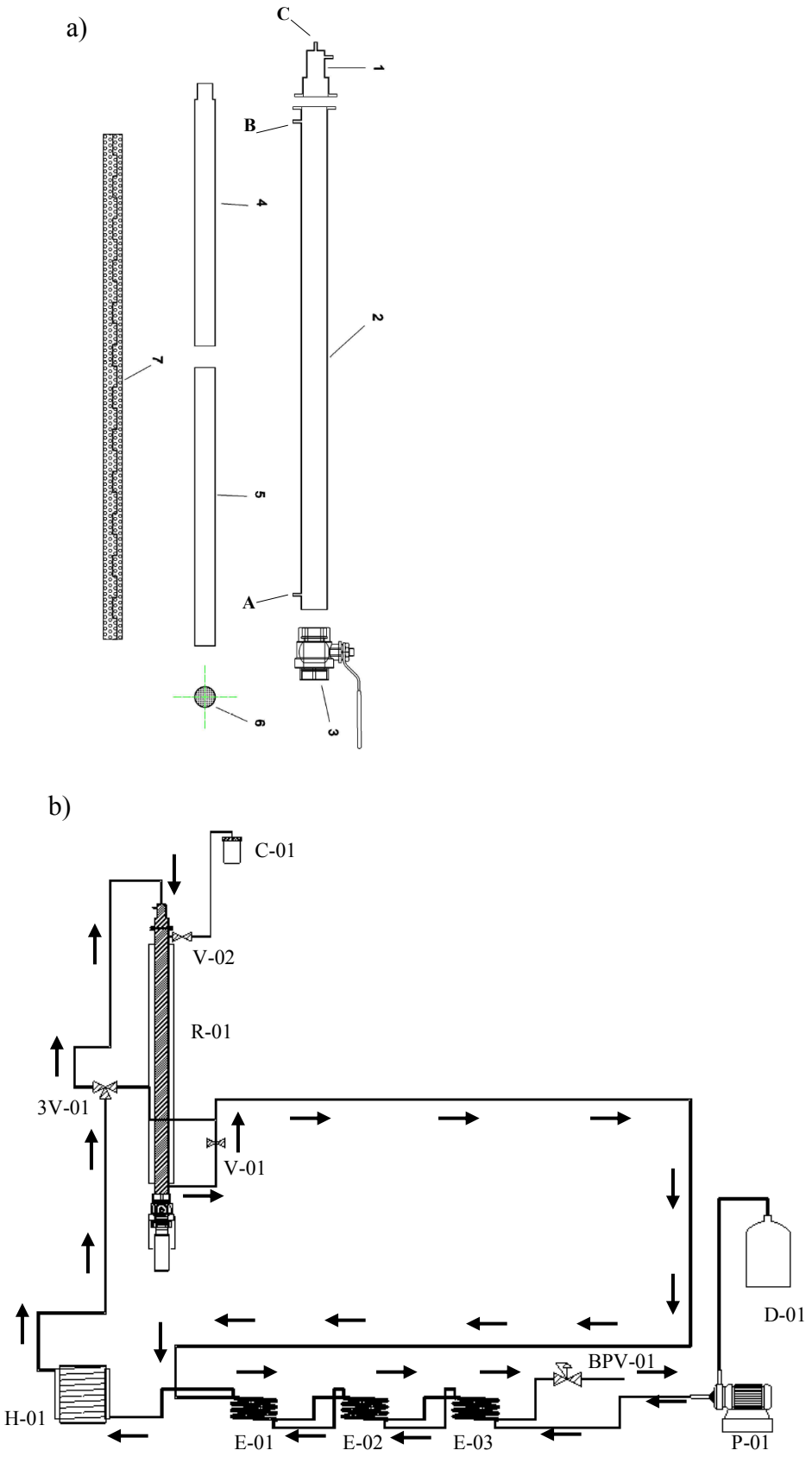
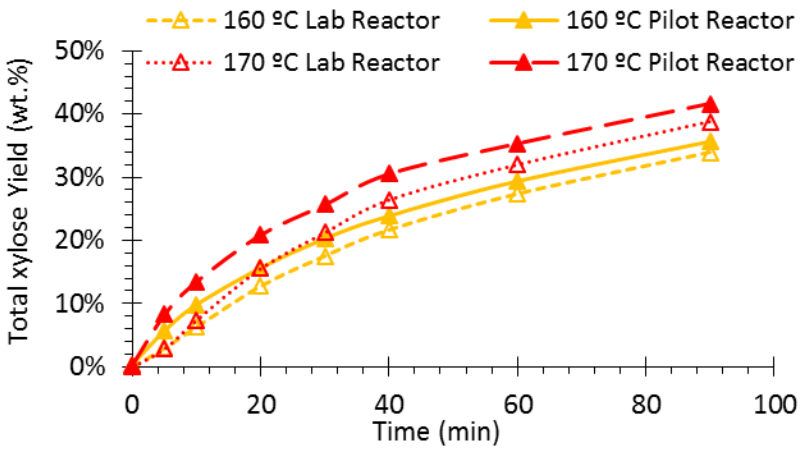
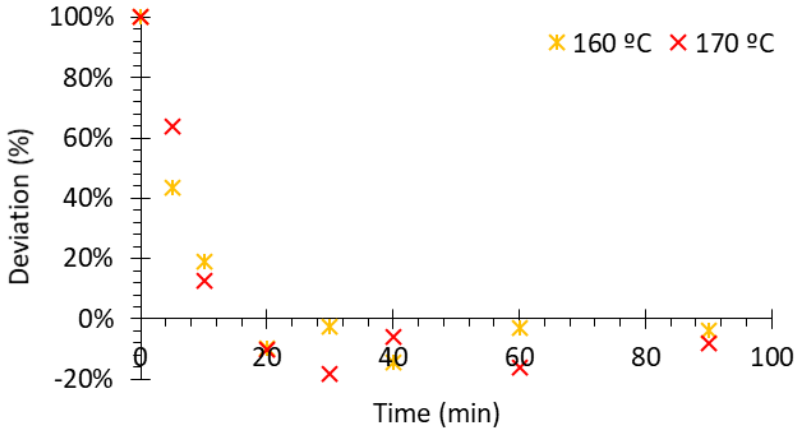

a)
C
1
B
4
2
7
5
A
6
3
b)
C-01
V-02
R-01
3V-01
V-01
D-01
BPV-01
H-01
E-01
E-02
E-03
P-01

Figure 3

a)


160 ºC Lab Reactor
160 ºC Pilot Reactor
170 ºC Lab Reactor
170 ºC Pilot Reactor
Total xylose Yield (wt.%)
50%
40%
30%
20%
10%
0%
0
20
40
60
80
100
Time (min)

b)


160 ºC
170 ºC
Deviation (%)
100%
80%
60%
40%
20%
0%
-20%
0
20
40
60
80
100
Time (min)

c)

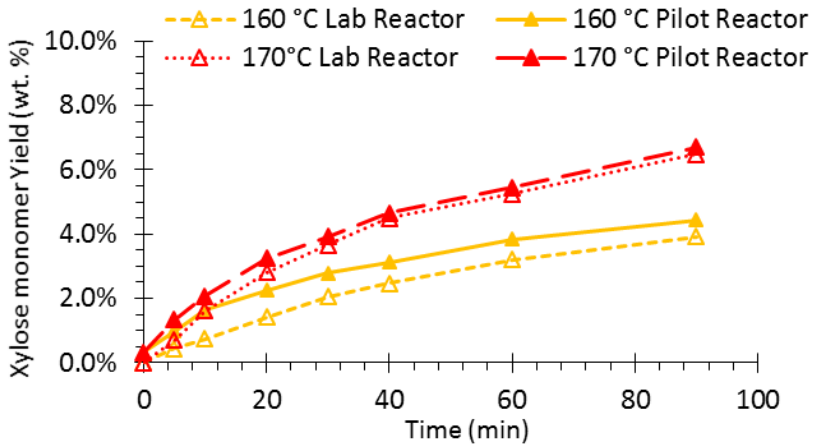

160 °C Lab Reactor
160 °C Pilot Reactor
170°C Lab Reactor
170 °C Pilot Reactor
Xylose monomer Yield (wt. %)
10.0%
8.0%
6.0%
4.0%
2.0%
0.0%
0
20
40
60
80
100
Time (min)

Figure 4

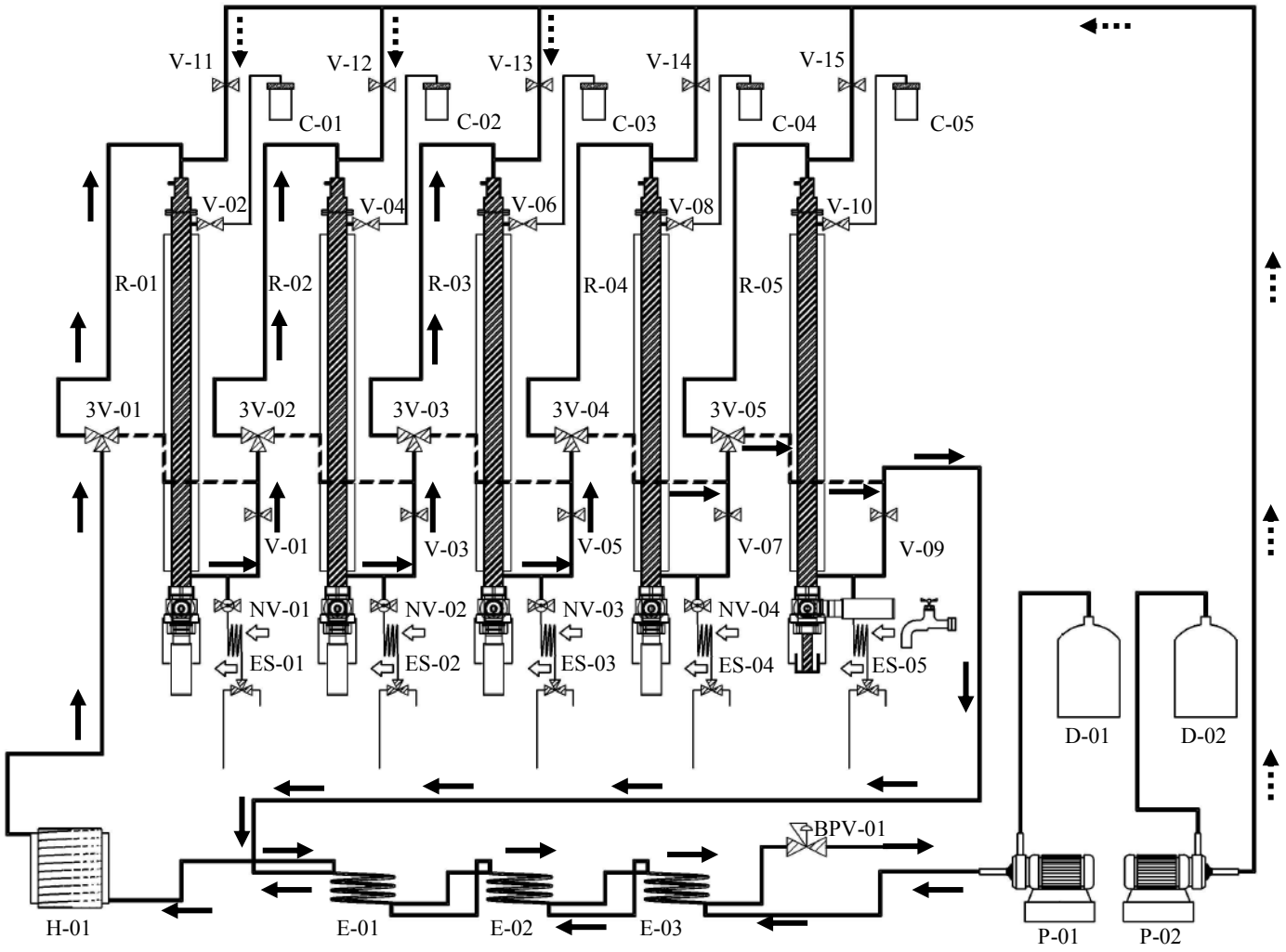
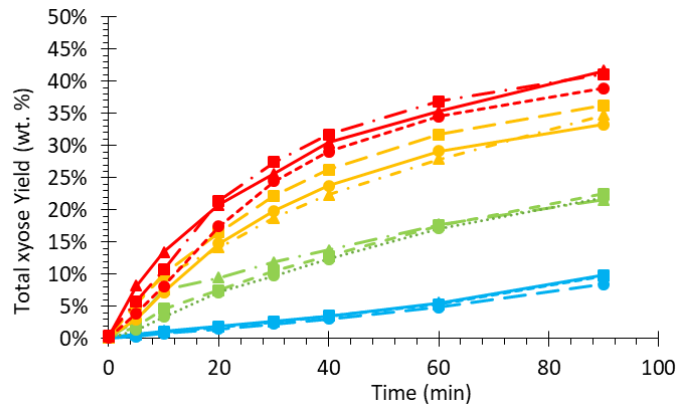

V-11
V-12
V-13
V-14
V-15
C-01
C-02
C-03
C-04
C-05
V-02
V-04
V-06
V-08
V-10
R-01
R-02
R-03
R-04
R-05
3V-01
3V-02
3V-03
3V-04
3V-05
V-01
V-03
V-05
V-07
V-09
NV-01
NV-02
NV-03
NV-04
ES-01
ES-02
ES-03
ES-04
ES-05
D-01
D-02
BPV-01
H-01
E-01
E-02
E-03
P-01
P-02

Figure 5

a)



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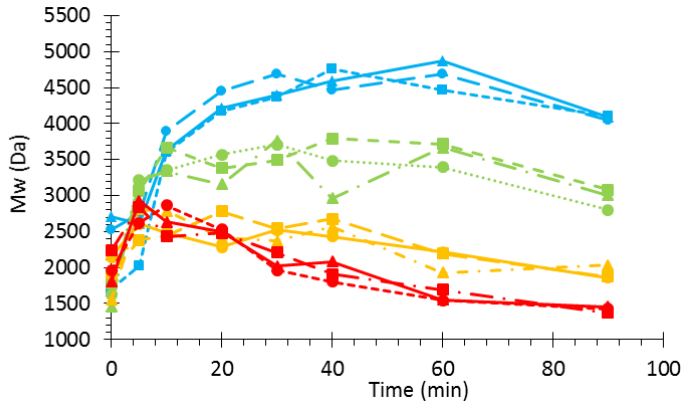

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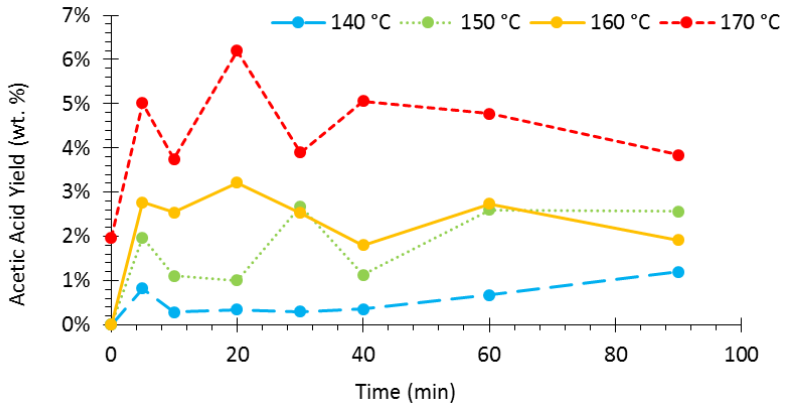

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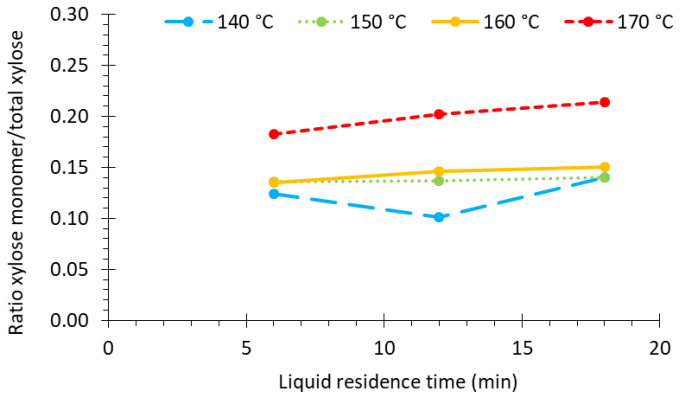
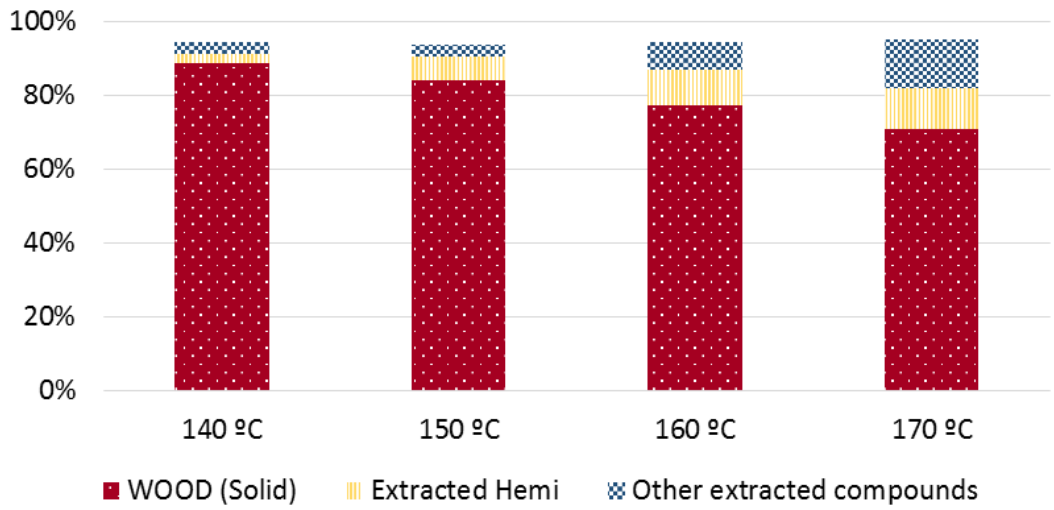


Figure 6.


100%
80%
60%
40%
20%
0%
140 ºC
150 ºC
160 ºC
170 ºC
WOOD (Solid)
Extracted Hemi
Other extracted compounds

Supplementary info

Click here to download Electronic Annex: Gallina_Supporting Material.docx