A Biorefinery Cascade Conversion of Hemicellulose-Free *Eucalyptus Globulus* Wood: Production of Concentrated Levulinic Acid Solutions for γ-Valerolactone Sustainable Preparation

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Abstract: *Eucalyptus globulus* wood samples were subjected to preliminary aqueous processing to remove water-soluble extractives and hemicelluloses, and the resulting solid (mainly made up of cellulose and lignin) was employed as a substrate for converting the cellulosic fraction into mixtures of levulinic and formic acid through a sulfuric acid-catalyzed reaction. These runs were carried out in a microwave-heated reactor at different temperatures and reaction times, operating in single-batch or cross-flow modes, in order to identify the most favorable operational conditions. Selected liquid phases deriving from these experiments, which resulted in concentrated levulinic acid up to 408 mmol/L, were then employed for γ-valerolactone production by levulinc acid hydrogenation in the presence of the commercial 5% Ru/C catalyst. In order to assess the effects of the main reaction parameters, hydrogenation experiments were performed at different temperatures, reaction times, amounts of ruthenium catalyst and hydrogen pressure. Yields of γ-valerolactone in the range of 85–90 mol % were obtained from the hydrogenation of the wood-derived solutions containing levulinic acid, obtained by single-batch operation or by the cross-flow process. The negative effect of co-produced formic acid present in crude levulinic acid solutions was evidenced and counteracted efficiently by allowing the preliminary thermal decomposition of formic acid itself.

Keywords: *Eucalyptus globules*; levulinic acid; γ-valerolactone; single batch and cross-flow processes; acid catalysis; ruthenium

1. Introduction

Fossil resources are currently employed as feedstocks for manufacturing a wide range of building blocks for further conversion into polymers, plastics, fuels and a number of fine and specialty chemicals [1,2]. Replacing the fossil resources by renewable materials (for example, lignocellulosic materials) contributes to the sustainable development of the chemical industry, fostering the development of a new bio-economy with favourable socio-economic and environmental implications. Lignocellulosic biomass is expected to play a key role in the future development of the chemical industry, as it is a major source of organic carbon that does not compete with the food

industry. Wood is the most abundant type of lignocellulosic biomass, and *Eucalyptus globulus* is a widespread, fast-growing species with high polysaccharide content.

The conversion of raw lignocellulosic materials into chemicals, fuels and products can be conveniently achieved following the biorefinery concept: the feedstocks can be subjected to different consecutive physico-chemical treatments to obtain separate streams containing "fractions" that can be valorized separately, in order to maximize the overall added-value of the starting substrate [3]. For example, the multistage fractionation of the feedstocks may provide the solubilisation of the hemicelluloses employing, for example, aqueous treatments with hot water, steam or diluted acids [4]. The solid phase recovered in this stage, mainly made up of cellulose and lignin, can be further processed for separating these components (for example, by delignification to obtain soluble lignin-derived compounds in liquid phase and cellulose as a solid phase; or by reactions aiming at the manufacture of soluble products from cellulose, in which lignin is left in solid phase). The conversion of cellulose into soluble products can be accomplished by a number of paths, including hydrolysis, hydrolysis–dehydration or hydrolysis–dehydration–rehydration.

According to these approaches, two chemical stages would be enough for obtaining the three structural components of the lignocellulosic biomass (or their respective reaction products) in separate streams: the first one provides a liquid phase containing hemicellulosic saccharides and a solid phase (enriched in cellulose and lignin), which can be employed in the second reaction stage to obtain soluble cellulose-derived products and an exhausted solid (mainly made up of lignin or lignin-derived products). Therefore, in this work, *Eucalyptus globlulus* wood has been first subjected to aqueous processing with hot-compressed water, in order to remove water-soluble extractives and convert the hemicellulosic fraction (mainly composed of substituted xylan, which contains a backbone of anhydroxylose units) into soluble saccharides (including pentoses and higher saccharides made up of anhydropentoses). The solubilized fraction can be used for a number of commercial biorefinery applications (for example, as prebiotics or for manufacturing xylose or furfural) [5,6]. The hemicellulose-free solid resulting from the aqueous processing of *Eucalyptus* wood has been treated in aqueous media in the presence of sulfuric acid, as catalyst. Under these conditions, lignin undergoes both hydrolysis and recondensation reactions, and is mainly recovered as a char-type, carbonaceous solid. On the other hand, cellulose is hydrolyzed into glucose, which goes to the liquid phase and is transformed in multiple products through a complex mechanism involving a number of series and parallel reactions [7–12]. The major reactions taking place can be summarized in the hydrolysis of cellulose into glucose; glucose isomerization into fructose via ketoenol tautomerization, followed by 5-hydroxymethyl-2-furaldehyde (HMF) generation from fructose and/or 1,2-diol intermediates; HMF rehydration into formic acid (FA) and levulinic acid (LA), both in equimolar amounts; and undesired side reactions yielding degradation and/or condensation products (humins) from some of the above compounds. On the other hand, the various species in the medium may react with other components (not derived from cellulose) present in the liquid phase (for example, products derived from residual hemicelluloses or acid-soluble lignin). Owing to the complex kinetics, the yields of the possible target products (HMF and/or mixtures of LA and FA) are usually significantly lower than the stoichiometric ones [4]. The distribution of products obtained within the acidic processing of model cellulose or lignocellulosic materials depends on a number of variables, including the type of catalyst and the temperature profile. In this regard, from one side, mineral acids (such as H_2SO_4, HCl, or H_3PO_4) show high catalytic activities, although they can be responsible for corrosion problems. In particular, sulphuric and phosphoric acids are widely used, this last being less efficient. Moreover, hydrochloric acid is also largely employed and it usually attacks biomass better than sulphuric acid but is more volatile [13]. On the basis of these considerations, the choice of sulphuric acid in the present investigation resulted in being the most appropriate for our purposes. On the other hand, up until now the employment of microwave heating on an industrial scale is still a challenge, despite considerable effort being expended in microwave process development. In this regard, the most significant drawbacks that have inhibited the industrial application of microwave

include the high cost of the equipment, the limited applicability, variation in dielectric properties with temperature, and the inherent inefficiency of electric power [14]. However, despite these limitations, microwave-assisted heating is considered an effective and sustainable tool at the laboratory scale for rapid initial screening before moving towards continuous processes which are more suitable for industrial large-scale plants. In particular, microwave absorption processes occur uniformly in the dielectric material, resulting in simultaneous heating of the whole volume of the sample, thus allowing better temperature homogeneity. Heat is directly transferred into the sample and the presence of the biomass containing polar oxygenated compounds in the reaction medium further contributes to the dielectric polarization. Interestingly, the carbohydrates show high microwave absorptivities that enable preferential heating [15,16]. In addition, the employment of microwave irradiation enables a higher heating rate, homogeneous heat distribution, efficient control, and remarkable energy and time saving [3,17–19].

The acidic processing of cellulose or cellulose-containing materials can be tuned to promote the formation of LA, a chemical with a bright future that has been included among the top-12 promising building blocks from biomass [19,20]. The chemistry of LA is rich owing to its multifunctional character, which enables the production of a wide range of chemicals. The catalytic hydrogenation of LA can be tuned to the formation of γ-valerolactone (GVL), a five-carbon cyclic ester that can be used as a building block for polymers, as an intermediate in the synthesis of fine chemicals, as a green solvent, as a food-flavoring agent, or as an additive for petroleum-derived fuels [20–23]. The LA conversion into GVL via heterogeneous catalysis is strongly affected by the type of catalyst. Literature studies indicate that Ru-based catalysts show high efficiency for hydrogenation [23–27], whereas significant conversions can be also achieved using catalysts containing other transition metals, such as Pt, Pd, or Ni [20,28–30].

Most literature has reported on the LA conversion into GVL operating on synthetic media (i.e., using solutions of commercial levulinic acid), but these results cannot be extrapolated to raw solutions coming from the processing of lignocellulosic materials, since these latter contain a number of potentially detrimental compounds, including the acid employed as a catalyst for LA generation, the FA obtained as a co-product, by-products from cellulose, and soluble contaminants derived from the other biomass fractions. The effects caused by these components can be reduced by implementing separation stages [31].

In this work, a multistage approach compatible with the biorefinery philosophy is proposed for *Eucalyptus globulus* wood exploitation. Wood was first subjected to aqueous processing (for removing water-soluble extractives and solubilizing hemicelluloses), and the resulting solid (enriched in cellulose and lignin) was employed as a substrate for acidic processing in single batch or cross-flow operations to obtain solutions containing LA and FA (resulting from the hydrolysis-dehydration-rehydration of cellulose). Finally, these solutions were employed to produce GVL from LA by catalytic hydrogenation in the presence of the commercial 5% Ru/C catalyst.

2. Results and Discussion

2.1. Autohydrolysis of Eucalyptus Globulus Wood

The composition of *Eucalyptus globulus* wood, expressed as weight percent over dry basis, was as follows: anhydroglucose units in cellulose, 44.9; anhydroxylose units in hemicelluloses, 16.6; anhydroarabinose units in hemicelluloses, 0.32; acetyl groups in hemicelluloses, 3.02; lignin, 23.2; extractives, 2.85; and other components (by difference), 9.17.

Aqueous processing caused an extensive removal of extractives and hemicelluloses, resulting in 61.1% yield of autohydrolyzed wood (AW), measured on an oven-dry basis with respect to the initial amount of solid. The major AW components were anhydroglucose units (accounting for 66.6% of the AW dry weight) and lignin (accounting for 30.2% of the AW dry weight). AW also contained small amounts of residual hemicelluloses and acetyl groups (which accounted for 2.25% and 0.37%

of the AW dry weight, respectively), and smaller amounts of other components. As reported in the literature [6], the liquid phase was largely composed of hemicellulose-derived saccharides (including monosaccharides, oligosaccharides and low-molecular weight polymers); whereas acetic acid (resulting from acetyl group hydrolysis) and minor amounts of furans, furfural (F) and HMF, were also present in these solutions. These experimental data confirmed that the aqueous processing of wood resulted in extensive hemicellulose solubilization with limited cellulose losses. Based on the solid yield and on the compositional data of wood and AW, it can be inferred that more than 90% of hemicelluloses were removed, while more than 90% of the original cellulose was retained in AW, thus confirming the suitability of this cascade approach for yielding the solid AW suitable for the further chemical conversion of its cellulosic fraction.

2.2. Production of Levulinic Acid (LA) and Formic Acid (FA) from Auto-Hydrolyzed Wood

2.2.1. Single-Batch Experiments

AW samples were treated in a microwave-heated reactor with sulfuric acid under different experimental conditions, in order to assess the effects of the main variables on the yield of the target products. Figure 1 shows the experimental results obtained operating at 190 °C.
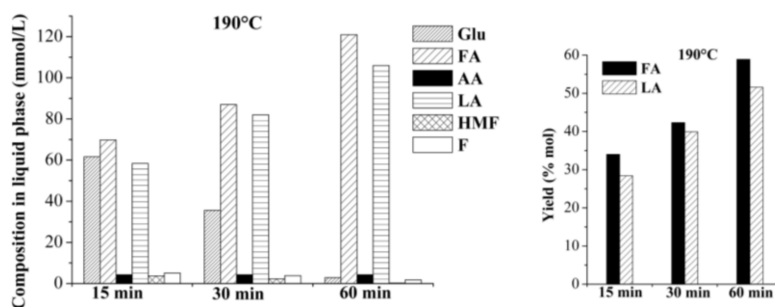

Figure 1. Concentration of polysaccharide-derived products obtained by sulfuric acid processing of autohydrolyzed wood (AW) in a microwave (MW) reactor at 190 °C (Glu: glucose; FA: formic acid; AA: acetic acid; LA: levulinic acid; HMF: hydroxymethylfurfural; F: furfural).

In the early stages of the experiment conducted at 190 °C, the hydrolysis of the cellulose contained in AW to give glucose was the most significant effect, giving a maximum glucose concentration of 61.6 mmol/L, after 15 min, whilst FA and LA yields were 34.1 and 28.5 mol %, respectively. By increasing the reaction time, glucose was progressively consumed up to near depletion after 60 min, whereas the yields of FA and LA obtained increased up to 59 and 52 mol %, respectively. Limited concentrations of furans (furfural and HMF) were also detected, indicating the low extent of occurred rehydration. In contrast to these last ones, whose concentration decreased during the advance of the reaction, acetic acid (AA) was a stable product from the hydrolysis of acetyl groups of biomass and its concentration remained constant at about 4.28 mmol/L during the whole reaction time.

Similar composition trends were observed for the experiment carried out at 200 °C reported in Figure 2, beyond the expected increase in the reaction rate.

As result of the faster cellulose hydrolysis, glucose concentration rapidly decreased during the experiment. After only 10 min, the yields of FA and LA were 52 and 48 mol %, respectively. The LA concentration reached a plateau after 20 minutes, with yields around 52 mol %. F and HMF behaved as reaction intermediates, reaching their maximum concentration in the early reaction stages and then undergoing further rehydration into FA and LA up to complete depletion.

It can be noted that the assays performed at 190 and 200 °C provided similar maximum yields of LA (about 52 mol %), which corresponds to a yield of about 37.2 wt % from cellulose and of about 15.0 wt % from the starting untreated biomass (*Eucalyptus globulus*) and FA (about 59 mol %), which

were reached after 60 and 25–30 min, respectively. The molar ratios FA/LA in both experiments were in the range 1.06–1.19. Even if the molar ratio FA/LA expected from the direct rehydration of HMF was 1/1, this parameter was also affected by other reactions taking place in the reaction medium, as reported in the literature. In fact, Flannelly et al. (2016) reported FA/LA ratios in the range 1.15 ± 0.08 for glucose treatments in acidic media, a range compatible with our results [32]. The ascertained yields to LA of the current work are in agreement with the results reported for cellulose hydrolysis in the presence of H_2SO_4 under MW heating [33] and for eucalyptus wood hydrolysis [34]. In this last case, a LA yield of 16.9 wt % based on the starting amount of eucalyptus wood was reported treating the initial biomass (200 g/L) in 0.2M H_2SO_4 solution at 170 °C under traditional heating for 5 h.

a: HMF: 0.3 mmol/L; b: furfural: 0.4 mmol/L;
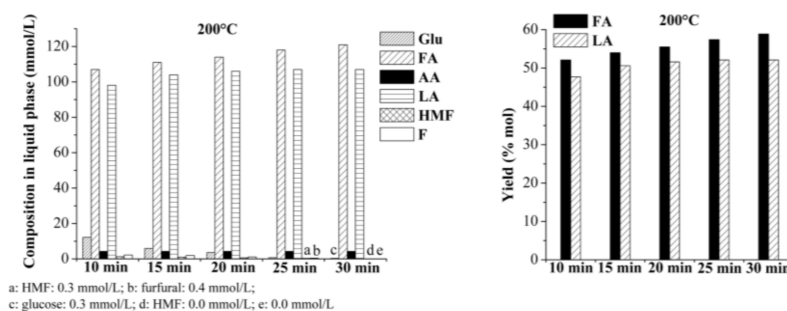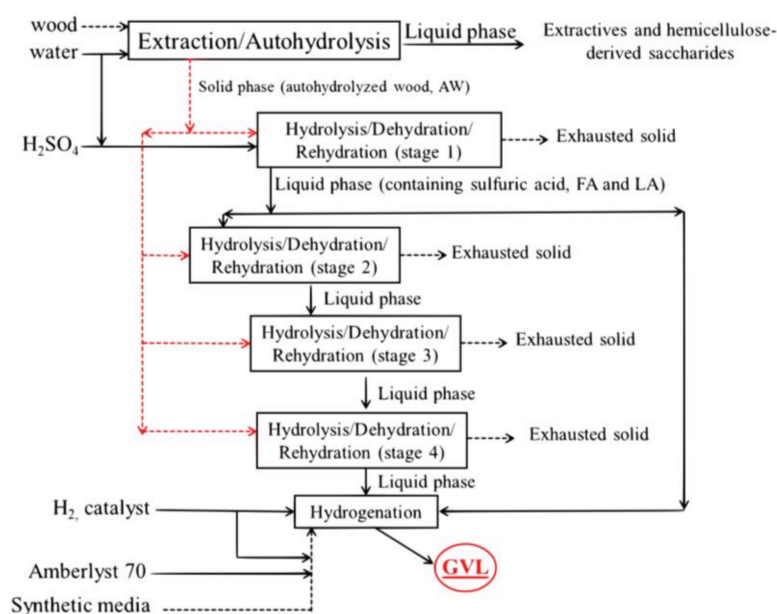c: glucose: 0.3 mmol/L; d: HMF: 0.0 mmol/L; e: 0.0 mmol/L

Figure 2. Concentration of polysaccharide-derived products obtained by sulfuric acid processing of AW in a MW reactor at 200 °C (Glu: glucose; FA: formic acid; AA: acetic acid; LA: levulinic acid; HMF: hydroxymethylfurfural; F: furfural).

2.2.2. Cross-Flow Batch Experiments

One of the main drawbacks of LA production from raw biomasses is represented by the low LA concentration, which limits the economic sustainability of the process [19]. With the dual aim of increasing the LA concentration and also reducing the amount of the employed sulfuric acid, three additional experiments were performed in cross-flow mode, as shown in Scheme 1.

Scheme 1. Scheme of the experimental work performed with wood and wood-derived fractions.

The liquid phase recovered from the experiment performed under selected conditions (stage 1, performed at 200 °C for 20 min) was employed to process fresh AW in the next experiment (stage 2). In the same way, stages 3 and 4 were performed using the liquid phase from the reaction obtained in stages 2 and 3, respectively. Since the exhausted solids leaving each stage has retained some liquid phase, the amounts of liquid fed to stages 2 and 3 were adjusted to keep the liquor-to-solid ratio at the fixed value of 20 g solution/g dried solid. The conductometric titration data showed that the sulfuric acid concentrations remained fairly constant after four reaction cycles. Figure 3 shows the results achieved in this set of experiments.
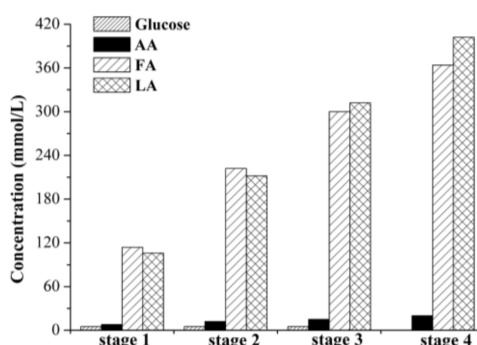

Figure 3. Composition of media obtained in experiments performed in cross-flow mode (for every stage T: 200 °C, reaction time: 20 min; glucose in stage 4 is absent).

Stage 1 was performed under the conditions shown in Figure 2 at 200 °C for 20 min, and the reutilization of this liquid phase in stage 2 doubled the LA concentration, keeping the LA yield constant (52.1 mol %). Stages 3 and 4 resulted in increased LA concentrations, respectively to 312 and 402 mmol/L. In comparison, the FA concentrations increased less than proportionally, in a way that the FA/LA molar ratio achieved in the first stage (1.07) decreased below 1 in stage 3, and dropped to 0.91 after stage 4. This experimental finding can be justified on the basis of the well-known susceptibility of FA to decomposition, which has been highlighted in the literature [24,35]. The concentrations of glucose were below 1.64 mmol/L in the solutions from stages 1 to 3, whereas no measurable amount of glucose was found in the solution from stage 4.

The results shown in Figure 3 evidence that this simple approach allows us to reach a significantly increased concentration in LA and suggest that working under harsh conditions causes a certain decomposition of FA. This aspect could be interesting because this compound is known to limit the performance of the metal catalysts employed in the LA hydrogenation into GVL. In order to confirm this statement, additional experiments were performed under harsher conditions, by treating fresh AW with the liquid phases from stage 3 at a higher temperature (220 °C instead of 200 °C) for longer reaction times (in the range 90–240 min). The results reported in Figure 4 are remarkable: heating at 220 °C for 90 min resulted in a markedly decreased FA concentration in comparison with the data shown in Figure 3 for stage 4 (from 364 to 123 mmol/L), whereas the LA concentration was slightly increased (from 402 to 408 mmol/L). Increasing the reaction time at 220 °C up to 120 or 180 min resulted in further FA losses (to achieve concentrations of 37.4 and 31.8 mmol/L, respectively) with a concentration of LA which remained unaltered at 408 mmol/L. In this set of experiments, the acetic acid concentration achieved was fairly constant (17.1 mmol/L), whereas no measurable amount of glucose remained in the reaction medium at the end of each experiment. Qualitative analysis of the gas phase recovered after 180 min. in this experiment (Figure 4) revealed the presence of CO_2. Work is now in progress to quantify the CO_2 and to clarify the decomposition reaction mechanism. In fact, the thermal decomposition of formic acid represents a well-known reaction which primarily may lead to the formation of CO and H_2O in the gas phase through the dehydration route, but also to CO_2 and H_2 in the aqueous phase through the decarboxylation one [36]. Water shows a strong effect on the two

decomposition pathways, reducing the activation barriers for both of them. The relative stability of the formic acid isomers, acid–water complexes and transition states plays an important role in determining the faster decomposition pathway, making water decarboxylation consistently more favourable than dehydration [37]. It is also important to highlight that the decomposition of formic acid occurs without the presence of catalyst: in this regard, the presence of a metal catalyst is not necessary but a thermal treatment is sufficient to promote the FA decomposition, thus avoiding contact of the catalyst with FA.
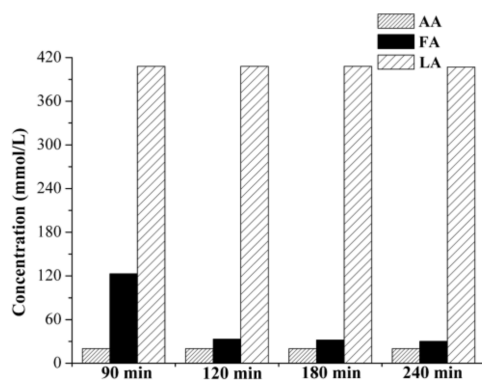

Figure 4. Results obtained in the experiments performed with the liquid phase deriving from stage 3 (see Figure 3) and fresh AW operating at 220 °C (glucose is absent).

2.3. γ-Valerolactone (GVL) Production

2.3.1. γ-Valerolactone GVL Production Using Crude Media from Autohydrolyzed Wood (AW) Processing in Single-Batch Mode

Extensive research has been performed on the hydrogenation of LA to GVL using homogeneous and mostly heterogeneous catalysts, especially supported metal catalysts, which have received considerable attention. Among them, Ru systems resulted in being the most active and selective for GVL formation [26,27,38,39]. In addition, the presence of an acidic co-catalyst promotes the susceptibility of the carbonyl group to hydrogenation into the intermediate 4-hydroxypentanoic acid, also favoring the final reaction step of GVL formation (ring closure) [23,40].

Even if abundant information has been reported on the hydrogenation of aqueous solutions containing pure LA, a limited number of studies have considered the presence of mineral acids in the LA-containing media obtained from lignocellulosic biomass [41,42]. Hydrogenation of LA-containing media resulting from the acidic processing of lignocellulosic materials is a complex issue, due to the presence of organic acids (including FA obtained as a reaction co-product and the acetic acid coming from the hydrolysis of the acetyl group), the acidic catalyst employed to achieve the hydrolysis–dehydration–rehydration of polysaccharides (in this work, sulfuric acid), and reaction by-products, such as humins and other soluble components derived from non-cellulosic fractions of the lignocellulosic feedstock, in particular soluble lignins. Since several of these products are able to deactivate metal-based catalysts, the hydrogenation in this type of media proceeds usually with limited GVL yields. The ability of metal-based catalysts to promote FA decomposition has been highlighted in the literature [43–45] and FA has been used as a hydrogen source to carry out the hydrogenation of LA in the presence of a Ru/C catalyst [24]. Both the presence of sulfuric acid and of coking effects negatively affected the downstream hydrogenation in the presence of Ru catalysts [42,46]. For this reason, the homogeneous acid catalyst and the co-product formic acid must be neutralized [9] or removed through combined solvent extraction and distillation. Both approaches severely limit the real direct "one-pot" route of conversion of biomass to LA and successive hydrogenation.

Crude media coming from the acidic processing of AW in single-batch mode under optimal conditions (stage 1, Figure 3: 200 °C, 20 min) were employed for hydrogenation. These solutions

contained, in addition to 114 mmol FA/L and 107 mmol LA/L, 0.104 mol of sulfuric acid/L, which is not consumed during the LA generation step.

Preliminary experiments (data not shown) were performed with acidic solutions from AW processing operating at 160 °C and 30 bar of H_2 pressure, using catalyst charges in the range 0.05–0.075 mmol of Ru. In this set of experiments, low LA conversions (below 13 mol %) were achieved even in long-lasting experiments (240 min), thus confirming the detrimental effects of the presence of sulfuric acid and contaminants in the medium. In order to improve these results, the reaction was carried out at 160 °C increasing the catalyst amount up to 0.1 mmol of Ru. The results in Figure 5A show that remarkably high GVL yields (up to 87.4 mol %) were obtained after a prolonged reaction time (240 min). In this experiment, the LA conversion was boosted in the period 60–150 min, concomitantly with an important drop in FA concentration. This can be explained on the basis of the negative effects caused by the presence of FA on LA hydrogenation, since formate ions can be adsorbed on the surface of Ru catalysts, limiting the available sites for LA hydrogenation, and delaying the GVL formation while the FA concentration remains high. This is in agreement with the results reported in the literature. In fact, Ruppert et al. [24] demonstrated that the addition of formic acid in the LA hydrogenation in the presence of 5% Ru/C carried out in water at 190 °C reduces considerably the catalytic efficiency. The authors rationalized this evidence taking into account the relative adsorption of the reactants computed by density functional theory (DFT) calculation. Formic acid can easily and strongly adsorb dissociatively on Ru particles in its formate form, whereas LA and dihydrogen have a much weaker energy of adsorption, resulting in the catalyst surface being fully covered by formate which acts as inhibitor for LA hydrogenation. In addition, Deng et al. [47] also hypothesized that the unreacted formic acid (or formate) poisoned the Ru/C catalyst employed in the hydrogenation of LA to GVL performed at 150 °C in water; the authors found that the inhibition effect did not disappear until the concentration of formic acid was markedly reduced. Finally, it is well-known that formic acid can not only promote side-reactions, but also can cause the leaching of metals into solutions [48].
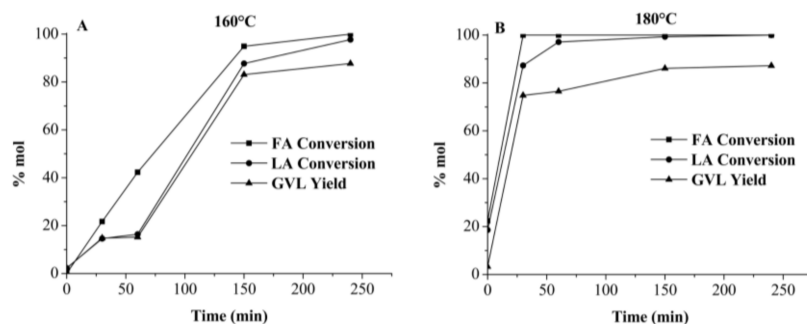

Figure 5. Results obtained in hydrogenation experiments using crude reaction media obtained in a single-batch operation. Reaction conditions: catalyst charge = 0.1 mmol Ru, P H_2 = 30 bar, initial LA and FA concentrations: 106.5 and 114.2 mmol/L. Reaction temperature: (**A**) 160 °C, (**B**) 180 °C.

In order to increase the reaction rate, an additional experiment was performed at a higher temperature (180 °C) using the same starting conditions. The results in Figure 5B show a fast FA decomposition, with almost complete LA conversion after 120 min, and a noticeable GVL generation (with yields of 74.7 and 86 mol % after 60 and 240 min, respectively).

2.3.2. GVL Production Using Crude Media from AW Processing Cross-Flow Operation

In order to obtain media with increased GLV concentration, hydrogenation of the LA solutions deriving from cross-flow operation was considered. The first set of experiments was performed with the solution obtained in the stage 4 of Figure 3 (composition: 0.104 M sulfuric acid, 364 mmol FA/L, and 402 mmol LA/L), operating at 160 °C with a hydrogen pressure of 30 bar for reaction time up to

390 min, using Ru charges of 0.15 or 0.25 mmol, and the results are shown in Figure 6. The experiment performed with 0.15 mmol of Ru (Figure 6A) was characterized by slow kinetics, with 35.4% decrease in FA concentration after 120 min, but just 12.4% LA conversion and 7.25 mol % GVL yield. When the reaction time was further increased up to 300 min, the FA concentration decreased significantly, but moderate variation was observed in the LA concentration, whereas some GVL generation from reaction intermediates took place, resulting in 11.5 mol % yield. In the experiment performed with 0.25 mmol of Ru (Figure 6B), the conversion and GVL yield significantly improved: FA was almost depleted after 390 min, and the LA conversion was boosted between 240 and 330 min (simultaneously to a marked drop of the FA concentration), resulting in 70.2 mol % GVL yield. When the reaction time was prolonged to 390 min, the GVL concentration increased to 342.7 mmol/L, corresponding to 85.2 mol % yield.
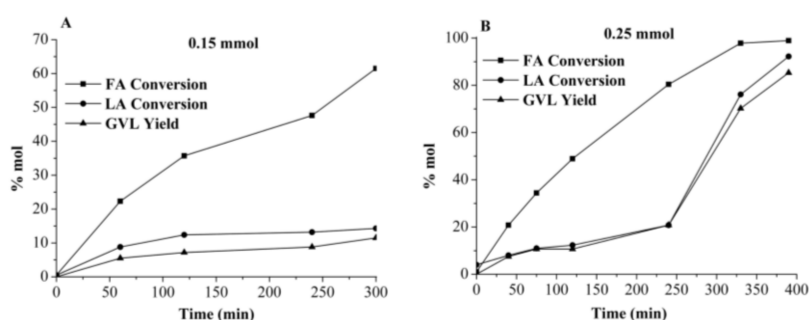

Figure 6. Results obtained in hydrogenation experiments performed with crude media coming from AW by cross-flow processing under the conditions of stage 4 of Figure 3. Reaction conditions: 160 °C, P H_2 = 30 bar, initial LA and FA concentrations: 402.0 and 364.1 mmol/L. Amount of catalyst: (**A**) 0.15 mmol, (**B**) 0.25 mmol.

The increased LA hydrogenation rate observed by decreasing FA concentrations led us to adopt as starting medium the reaction solution obtained by cross-flow approach (stage 3, Figure 3) with a treatment at 220 °C (as reported in Figure 4), which is characterized after 180 min by a low FA/LA ratio. The results obtained are reported in Figure 7. The first experiment was performed at the best catalyst charge identified in the experiments shown in Figure 6B, at the same temperature (160 °C) and hydrogen pressure. Comparison of the achieved results (reported in Figure 7A with those shown in Figure 6B) confirmed that the adoption of this reaction medium improved the reaction rate, with 72.7 mol % GVL yield after just 30 min (in comparison with 330 min needed for achieving the same GVL yield in the former experiment). Based on this, an additional experiment (see Figure 7B) was performed to assess the behavior of the system at a lower temperature (130 °C). The assay at 130 °C with 0.25 mol Ru resulted in slower kinetics, but it is remarkable that the maximum GVL yield (achieved after 200 min) was 89.8 mol %, a noticeable result considering that a crude reaction medium directly obtained from acid-treated raw biomass was involved.
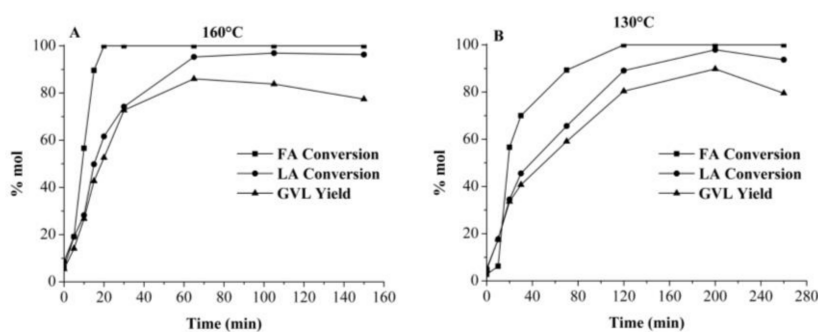
Figure 7. Results obtained in hydrogenation experiments performed on crude media coming from AW by the cross-flow approach (stage 3, Figure 3) with a treatment at 220 °C for 180 min. (as reported in Figure 4). Reaction conditions: catalyst charge = 0.25 mmol Ru, P H$_2$ = 30 bar, initial LA and FA concentrations: 407.1 and 31.8 mmol/L. Reaction temperature: (**A**) 160 °C, (**B**) 130 °C.

2.3.3. Catalyst Characterization before and after Reaction

It is well-known that the activity and the selectivity achieved for a heterogeneous catalytic reaction depends, among other factors, on the structural, geometric, morphological and electronic properties of the catalyst employed [49]. For that reason, the fresh commercial 5% Ru/C catalyst was characterized by transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) analysis. The sample resulted homogeneous in particle distribution and size, with the Ru average diameter being 1.5 nm with a surface area of 802 m^2/g, values in perfect agreement with the literature [50]. In order to make a process sustainable, a very important aspect to be considered in heterogeneous catalysis is the stability of the catalyst for reuse without significant decreases in activity and selectivity. Therefore, the metal particles' aggregation which can occur during the reaction must be properly evaluated because it is usually followed by the catalyst's deactivation. In this regard, the spent catalyst (commercial 5% Ru/C) employed in the experiment carried out at 130 °C with 0.25 mmol Ru (see Figure 7B) was compared with the fresh one. Figure 8 reports the TEM micrograph and particle size distribution of the spent 5% Ru/C catalyst employed in the run carried out at 130 °C with 0.25 mmol Ru described in Figure 7B.
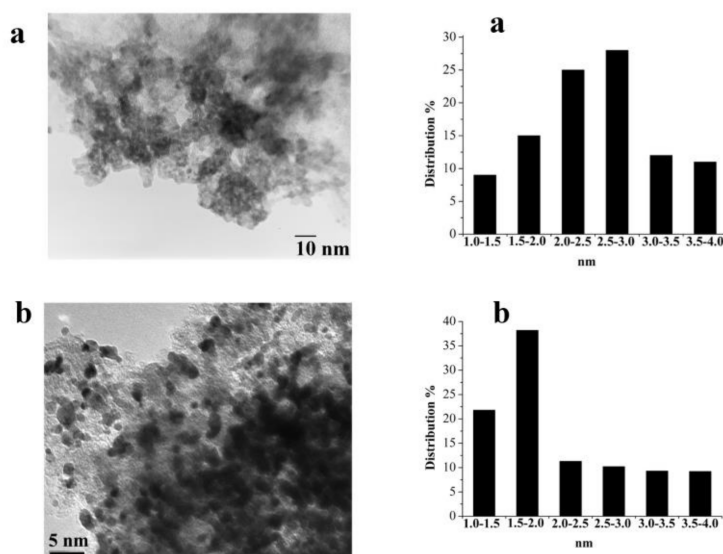

Figure 8. (**a**) Transmission electron microscope (TEM) micrograph and particle size distribution of spent 5% Ru/C employed in run carried out at 130 °C with 0.25 mmol Ru; (**b**) TEM micrograph and particle size distribution of fresh 5% Ru/C.

After use, the Ru/C catalyst showed a little increase in the Ru particle size and a slight decrease of the surface area, resulting in the Ru average diameter and surface area being 2.5 nm and 797 m^2/g, respectively, in comparison with 2.1 nm and 900 m^2/g of the fresh catalyst. The results obtained suggest that the commercial catalyst presents a little sintering effect at the end of the reaction, highlighting its robustness and thus the feasibility of the employed cascade approach directly from crude media. Finally, the leaching of ruthenium in the reaction media obtained at the end of the catalytic run carried out at 130 °C with 0.25 mmol Ru (see Figure 7B) was determined by inductively coupled plasma (ICP) analysis. Under the reaction conditions employed, the absence of leaching was ascertained, thus allowing us to exclude its dissolution in the aqueous phase.

3. Materials and Methods

3.1. Materials

Eucalyptus globulus wood samples were kindly provided by ENCE (Pontevedra, Spain). Samples were air-dried, milled to pass an 8 mm screen, homogenized in a single lot to avoid compositional differences among samples, and stored until use.

Levulinic acid, formic acid, sulfuric acid and the 5% Ru/C catalyst (average diameter: 2.1 nm and surface area: 900 m^2/g), employed in this study, were purchased from Sigma Aldrich (Saint Louis, MO, USA).

3.2. Aqueous Processing of Wood

Eucalyptus globulus wood samples were first subjected to an aqueous extraction under non-isothermal conditions at 130 °C to remove water-soluble extractives without altering the polysaccharide fractions, as proposed in an earlier work [6]; and the pre-extracted solid was subjected to auto-hydrolysis (using water as the sole reagent) operating in a 3.75 L stainless steel reactor (Parr Instrument Co., Moline, IL, USA) at a liquid-to-solid ratio of 8 kg water/kg of oven-dry raw material. In auto-hydrolysis experiments, the reaction media were stirred at 150 rpm and heated up to reach 210 °C, considered as the optimal condition for reaching a selective solubilization of hemicellulose while causing minimal effects on cellulose and lignin. The choice of the experimental conditions was based on previous experiments exploring the best range reported in literature [51]. The reaction media was filtered, and the solid phase (here denoted autohydrolyzed wood, AW) was employed as a substrate for acid-catalyzed conversion.

3.3. Wood and Solid Analysis

Wood was assayed for ethanol extractives using the TAPPI 264 method; and both wood and AW were analyzed for moisture (by oven-drying at 105 °C until constant weight) and subjected to quantitative acid hydrolysis (TAPPI 249 method) before gravimetric determination of lignin and high-performance liquid chromatography (HPLC) analysis of sugars and acetic acid (measuring the contents of polysaccharides and acetyl groups linked to hemicelluloses, respectively).

3.4. LA Production from AW in Acidic Media

Air-dried AW samples were mixed with sulfuric acid (0.102 mol acid/L) to achieve the desired solid (dry AW) to liquid (acidic solution) weight ratio of 1 g/20 g in 100 mL Teflon vessels fitted with magnetic drive stirrers, and the suspensions were heated in a Microwave Accelerated Reaction System (MARS 6, CEM Corporation, Matthews, NC, USA) and kept at the target temperature for the desired reaction time. In addition, AW was subsequently processed in three additional experiments with acidic solutions from previous treatments according to a cross-flow scheme. Scheme 1 summarizes the experimental plan considered in this study for the processing of wood and wood-derived fractions. Temperature (in the range 200–220 °C) was controlled by optical fiber and IR sensors; whereas one vessel, used as a reference, also contained a pressure sensor. The samples were heated up to the desired

temperature, kept under isothermal conditions for the desired reaction time, and then cooled. Aliquots from the liquid phase were assayed for composition by HPLC. The solutions were employed for GVL production by hydrogenation or for further treatment of AW in the cross-flow approach (see Scheme 1).

3.5. LA Hydrogenation to GVL

Hydrogenation experiments were carried out by contacting H_2 with biomass-derived media containing LA in the presence of a commercial heterogeneous 5% Ru/C catalyst. The catalyst charges employed (which are referred to a total reaction volume of 40 mL) were in the range 0.1–0.25 mmol of Ru. Assays were performed in a 300 mL stirred Parr 452HC3/ZR702 reactor (Parr Instrument Company, Moline, IL, USA) made of zirconium grade 702 fitted with temperature and stirring controls.

The desired amount of the catalyst was placed in the reactor, which was subjected to repeated cycles of evacuation and N_2 flushing to ensure complete oxygen removal, and then the starting solution was introduced by suction. Hydrogen was supplied to achieve the desired pressure (10 or 30 bar), which was maintained manually along the reaction. Isothermal conditions (temperatures in the range 130–210 °C) were maintained for the desired reaction time (up to 420 min). In each experiment, time zero was taken at the beginning of the isothermal stage. Samples of the liquid phase were withdrawn periodically through the sampling valve during the reaction, quickly cooled and analyzed by HPLC. After the reaction, the reactor was immediately cooled down to room temperature and the gas phase was released to a reservoir for measuring the volume of evolved gas with a gas meter.

3.6. Analytical Methods and Structural Characterization

The liquid phases from quantitative acid hydrolyses of wood or AW were filtered through 0.45 μm polytetrafluoroethylene (PTFE) membranes and analyzed by HPLC using an Agilent 1100 instrument (Agilent Technologies, Santa Clara, CA, USA) fitted with a refractive index detector. Concentrations of higher saccharides and bound acetyl groups in autohydrolysis liquors were measured from the increases in the concentrations of monosaccharides and acetic acid observed after performing a quantitative post-hydrolysis (NREL/TP-510-42623 method). Monosaccharides (glucose, xylose and arabinose), acetic acid, FA, furfural, HMF and LA were determined using a 300×7.8 mm Aminex HPX-87H column (BioRad, Life Science Group Hercules, Hercules, CA, USA) and a guard column kept at 50 °C. The mobile phase (0.006 N H_2SO_4) was eluted at 0.6 mL/min.

Monosaccharides, acetic acid, FA, furfural, HMF, LA and GVL in media resulting from hydrogenation were determined by HPLC using a Perkin Elmer Flexar Isocratic Platform (PerkinElmer, Waltham, MA, USA) equipped with a refractive index detector and a Benson Polimeric 2000-VP-OA column (300×7.8 mm). The column was thermostated at 60 °C, and the mobile phase (0.005 M H_2SO_4) was eluted at 0.6 mL/min. The concentration of sulfuric acid was determined by conductometric titration, based on its strong acidic character (in comparison with the weak acidity of the other acids present in the media).

Qualitative analysis of the composition of the product gas was performed employing a Perkin Elmer Autosystem XL gas chromatograph (PerkinElmer, Waltham, MA, USA) equipped with a thermal-conductivity detector. The stainless steel column Unibeads C (4 mm $\times$ 2 m) was employed, keeping the column temperature at 60 °C and the flow rate of helium at 33 mL/min.

Inductively coupled plasma optical emission spectroscopy analysis (ICP-EOS) was performed with a Spectro-Genesis instrument (Spectro Analytical Instruments GmbH, Cleves, North Rhine-Westphalia, Germany) equipped with the software Smart Analyzer Vision (version 4, Spectro Analytical Instrument GmbH, Cleves, North Rhine-Westphalia, Germany).

TEM imaging was carried out using a Philips CM12 microscope (Philips, Amsterdam, North Holland, The Netherlands) working at 120 kV. Histograms of the particle size distribution were obtained by counting at least 500 particles on to the micrographs.

4. Conclusions

Adopting a multi-valorization approach, *Eucalyptus globulus* wood samples were treated with hot, compressed water for fractionation purposes, to yield both a valuable solution containing extractives and hemicelluloses and a solid auto-hydrolyzed wood, keeping more than 90% of the cellulose contained in the original wood. This auto-hydrolyzed wood was mixed with water in the presence of sulfuric acid and processed in a microwave-heated reactor to convert the cellulosic fraction into mixtures of formic acid and levulinic acid. This acid conversion was performed both in single batch or cross-flow operation in the presence of 0.104 M sulfuric acid, in order to obtain reaction media with different concentrations of levulinic acid. With respect to the single batch, the cross-flow allowed us to obtain much more levulinic acid-concentrated reaction media.

The hydrogenation of crude media from a single-batch operation was performed and γ-valerolactone yields above 87 mol % were reached in experiments at 160 and 180 °C, under 30 bar of hydrogen. Remarkably, the negative effect of co-produced formic acid present in crude levulinic acid solutions was softened, by allowing the preliminary thermal decomposition of formic acid itself, leaving levulinic acid-rich aqueous solutions for cascade hydrogenation. In fact, the hydrogenation of crude media from the cross-flow operation with a low formic acid/levulinic acid ratio, deriving from a formic acid thermal decomposition step before hydrogenation, proceeded with comparatively faster kinetics, resulting in a high γ-valerolactone yield (89.8 mol %) operating at 30 bar of hydrogen at lower temperature (130 °C). Thus, this simple approach favored a high γ-valerolactone yield directly from crude media in the presence of a Ru/C commercial catalyst, without intermediate steps of neutralization or extraction. The Ru leaching into the reaction solution was excluded by ICP analysis as well as sintering by a TEM investigation.

Author Contributions: All the authors conceived and designed the experiments; Sandra Rivas performed the experiments and analysis, all the authors analyzed the data and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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