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Acid-catalyzed fractionation of almond shells in γ-valerolactone/water

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Abstract
The fractionation of almond shells, an agro-industry residue available in some Mediterranean climate regions, was investigated using acid-catalyzed hydrolysis in γ-valerolactone(GVL)/water. A set of non-isothermal experiments at nominal temperatures of 120, 140 and 160 °C and sulfuric acid concentrations from 25 to 75 mM were developed using a constant 80% w/w GVL in water concentration and a reaction time of up to 120 min. GVL was an efficient media and promoted solubilization of both lignin and hemicellulose, even at low temperature during the initial period of reactor heating, while cellulose conversion was limited. A temperature of 160 °C gave the highest extraction of lignin and hemicellulose, but recovery of hemicellulose carbohydrates was better below 140 °C. Sulfuric acid concentrations above 45 mM promoted excessive dehydration of xylose and glucose to furans and humins, which were recovered with lignin. A model was developed to describe the kinetics of lignin and hemicellulose solubilization. It distinguished three fractions of different reactivity in each polymer (lignin or hemicellulose): fast-reacting, slow-reacting and unreactive. The amount of each fraction was correlated with acid concentration and reaction temperature. Activation energies and the other parameters in the model were obtained numerically by least-squares optimization using the data from the non-isothermal experiments. Activation energies for the fast- and slow-reacting fractions of hemicellulose were 142. and 39.7 kJ mol^{-1}, and for those of lignin 134. and 71.7 kJ mol^{-1}, respectively. Acid concentration had a larger influence than temperature on establishing the amounts of slow-reacting hemicellulose and lignin, whereas temperature was the dominant variable concerning the fractions of non-reacting polymers.

Keywords: almond shells · organosolv fractionation · kinetic modeling · delignification

DECLARATIONS

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The authors declare that they have no conflict of interest.

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Author's contributions

- Arianna Corti: planning and development of the fractionation experiments. Data processing and discussion of results.
- Esther Torrens: development of the analytical methods and technical support. Revision of the manuscript.
- Daniel Montané: planning of the fractionation experiments. Data processing, modeling and discussion of results. Manuscript preparation and writing. Final edition.

1 Introduction

Lignocellulosic biomass is a generic term that designates the organic matter produced by terrestrial plants. It is composed of three biogenic polymers, cellulose, hemicellulose and lignin, which form the walls of the vegetal cells. Technically, lignocellulosic biomass includes byproducts from the forest industry, residues from agroindustry and short rotation non-edible crops like switchgrass and miscanthus, but also unusable streams from paper recycling and some fractions derived from municipal solid waste can be included in this wide category of bioresources.

Research on alternatives to fossil resources for fuels and feedstocks for the chemical industry has demonstrated the feasibility of converting lignocellulosic biomass into chemicals and liquid fuels through biorefining [1-4]. Biorefineries based on lignocellulosic feedstocks involve the combination of multiple chemical and biological processes to produce higher value-added products due to the low susceptibility of this type of biomass towards enzymatic and fermentative conversion. Most arrangements start with a pretreatment step aimed at breaking down the cell wall structure to facilitate the separation of lignin and hemicellulose from cellulose [5, 6]. This reduces the crystallinity of cellulose and increases its accessibility to enzymes and microorganisms thus facilitating bioconversion, but also produces lignin and hemicellulose streams that can be processed further into marketable products [7]. Among several existing methods, organosolv pretreatments are suitable for biomass fractionation because they produce highly delignified cellulose, allow the recovery of hemicellulose sugars, and yield technical-grade lignin that retains most of its native structure and reactivity [4, 7-9]. Due to their delignification effectiveness, organosolv pretreatments are probably the best option to deal with highly lignified biomasses, such as softwood species [5]. Organosolv processes involve the use of water-miscible organic solvents with or without catalysts. The latter are usually mineral acids, but some base catalysts can also be used. Recently, the bio-derived solvent γ-valerolactone (GVL) has received significant attention as organosolv media because it accelerates the rates of acid-catalyzed hydrolysis over the reactions of carbohydrate dehydration when compared with water, thus favoring the recovery of hemicellulose and cellulose while promoting lignin extraction at mild conditions of temperature and concentration of acidic catalysts [10-12]. Moreover, lignin can be precipitated and recovered from GVL/water mixtures through addition of water.

Temperature is a key parameter in organosolv processing with GVL/water. Hardwood lignin was found to be recalcitrant to delignification in 80% w/w GVL below 110 °C using heteropoly acids as catalysts, but 130 °C provided the optimal conditions in terms of delignification and prevention of cellulose degradation [13]. Likewise, a temperature of 120 °C was enough to achieve 80% delignification of hardwood using 75 mM sulfuric acid as catalyst [14]. According to Trevorah and co-workers [15] during the sulfuric acid-catalyzed hydrolysis of Eucalyptus wood some bonds in the lignin structure could only be broken at ca. 150 °C or above, but at 180 °C more than 60% of cellulose was hydrolyzed and dissolved in 50% w/w GVL, even with only 0.5 h of reaction time. Most studies on biomass fractionation in GVL/water use temperatures comprised between 120 and 160 °C [13-18]. In this range, efficient biomass delignification can be achieved while minimizing carbohydrate degradation, provided that the concentration of acid catalyst is adjusted to adequate values.

Acid catalysis is preferred in GVL/water processing, sulfuric acid being the mineral acid of choice due to its high catalytic activity even at relatively low temperature. Acid concentration has to be selected carefully to balance the efficiency in delignification with a limited degradation of carbohydrates. Hardwood hydrolysis in 80% w/w GVL at 120 °C for up to 2 h achieved higher delignification and xylan solubilization with 75 mM H_2SO_4 than with 25 mM, while glucan was barely affected in either case [14]. However, bamboo hydrolysis in 60% w/w GVL at 140 °C with 50 mM H_2SO_4 promoted the solubilization of ca. 20% of cellulose after only 20 min of operation [18]. Sulfuric acid concentrations above 100 mM are seldom used for biomass fractionation in GVL/Water to minimize the solubilization of glucose [14-18]. Reaction time ranges between 20 min and 5 h, but durations from 1 to 2 h are common [13-18]. Depending on the other operating parameters, however, extended reaction periods may be undesirable since they promote the degradation of carbohydrates over lignin solubilization. At short reaction time delignification and hemicellulose removal are generally fast regardless of the biomass being treated, but after ca. 1 h lignin removal becomes slower, the hemicellulose-derived carbohydrates start to dehydrate and degrade, and cellulose also starts to decompose significantly [14-16].

The GVL/water ratio has a strong impact on the efficiency of the fractionation process. Lê and co-workers [11], after testing GVL:water mass ratios from 0:100 to 100:0 at 180 °C for 2h without acid addition, reported that a GVL content from 50 to 60% w/w gave optimal lignin and xylan solubilization, but 80% w/w gave lower cellulose hydrolysis with similar results concerning delignification and hemicellulose extraction. An 80% w/w GVL also gave the highest extraction of lignin and hemicellulose in the fractionation of Cotton stalk with 10 mM sulfuric acid at 170 °C and yielded cellulose with the highest accessibility towards enzymatic saccharification [19]. A lignin removal of up to 80% was also reported with an 80% w/w GVL while cellulose could be preserved in the hydrolyzed solid and easily converted by subsequent enzymatic treatments [14, 16]. In general, a GVL concentration close to 80% w/w seems to provide an adequate balance between the need of a high amount of GVL to solubilize lignin, and the requirement of enough water to be present to facilitate the dissociation of the acid catalysts to promote hydrolysis.

Almond shells (AS) are an agroindustry byproduct available in the Mediterranean region of Spain, which accounts for ca. 4% of the worldwide production of almonds. The shells constitute over 50% of the dry mass of the almond fruits and correspond to the endocarp that is formed mostly by isodiametric stone cells with thick and highly lignified walls [20]. Conventional fractionation of AS in aqueous phase by successive acid prehydrolysis and soda delignification proved challenging due to the high lignin content and density of this biomass. Maximum lignin extraction efficiencies of ca. 50% were obtained at the prehydrolysis conditions that maximized hemicellulose recovery [21, 22]. Given the versatility of acidic GVL/water for biomass fractionation and the particular physicochemical characteristics of AS, it was deemed of interest to investigate the suitability of this organosolv system for AS processing. To our best knowledge, no previous study on the fractionation of almond shells with acidic GVL/water has been previously conducted. In this paper, experiments have been carried using a mixture of GVL and water with a constant mass ratio of 80:20 and sulfuric acid concentrations from 25 to 75 mM. Nominal temperatures of 120, 140 and 160 °C have been tested, although the experiments were non-isothermal since biomass was partially hydrolyzed during the reactor heating stage. The effect of each parameter on the conversion of the constitutive

polymers of AS into soluble products has been assessed, and a kinetic model has been proposed to describe the rates of conversion of hemicellulose and lignin.

2 Experimental

2.1 Materials

Ground Almond shells were provided by MIMSA (Lleida, Spain) as a powder with an average particle size of 300 µm (product reference HC-TC3). The material had an average humidity of 7.6% and was used as received. Mixtures of deionized water with GVL (≥ 99%, Sigma Aldrich) were used as reaction media with sulfuric acid (2.5 M, PanReac) added as catalyst. Ethanol (≥ 99.8%, Sigma Aldrich) was employed to determine the organic extractives of the native almond shells. Standards for the HPLC analysis of the hydrolysis products were prepared for D(+)-glucose (≥ 99.5%, Sigma Aldrich), D(+)-xylose (≥ 99%, Merck), L(+)-arabinose (≥ 99%, Merck), furfural (≥ 99%, Sigma Aldrich), acetic acid (≥ 99%, Sigma Aldrich) and levulinic acid (≥ 99%, Sigma Aldrich). All chemicals were used as received.

2.2 Reaction procedure

A total of 45 experiments were performed at a constant GVL:water mass ratio of 80:20, sulfuric acid concentrations of 25, 35, 45, 50 and 75 mM, nominal temperatures of 120, 140 and 160 °C and a reaction time from 15 to 120 min. The experiments were non isothermal and reaction time included the heating period from room temperature to the nominal temperature, as detailed below. All experiments were performed under autogenous pressure, which was below 7 bar(a) at 160 °C.

Reactions were carried out in stirred batch reactors having a nominal volume of 30 mL. The reactors were constructed using commercial 316-grade stainless steel tubing fittings (Ham-Let). They mounted an internal thermocouple (1/16-inch K-type) connected to a data acquisition system based on LabView (National Instruments) to record the temperature profile of each experiment, a pressure indicator, a safety pressure relief valve set at 70 bar, manually operated valves for purge and depressurization, and a magnetic stirrer to homogenize the slurry of powdered almond shells during the reaction. In each experiment, the required amounts of GVL, deionized water and 2.5M sulfuric acid (15 mL total volume) and ca. 1.5 g of powdered almond shells were loaded into the reactor. The vessel was then mounted on a vertically sliding support and sealed, purged with nitrogen to remove oxygen, and pressurized to 10 bar(g) at room temperature to check for the absence of leaks. Pressure was then released slowly through a manual purge valve and the vessel was lowered into a bath of silicone oil (LBSil 100 AUX, Labkem) mounted on top of a heating plate (IKA RCT), which was preheated at the desired reaction temperature. Once the reactor rested on the heating plate, stirring was started and adjusted to 900 rpm. When the required reaction time had been elapsed, the reactor was raised from the oil bath and rapidly immersed in a water bath at room temperature to quench the reaction. Residual pressure was then carefully released through the purge valve and the reactor vessel was detached from the support. The heating rates in this system were moderate. Figure 1 shows the temperature profile of a 120 min long experiment at a nominal temperature of 120 °C, which was characterized by a relatively rapid heating period until ca. 115 °C followed by a

nearly isothermal period afterwards. This figure also illustrates the good reproducibility of the temperature evolution during the heating period with two shorter experiments performed at the same nominal temperature. In general, the time required to reach 95% of the nominal temperature of the experiment was ca. 30 min, during which a significant degree of biomass hydrolysis was already achieved. Thus, reaction time was taken as the time elapsed from the instant the reactor was introduced into the oil bath to the moment in which it was extracted. Furthermore, recording of the time-temperature history of each experiment was deemed necessary to validate that all data points obtained at the same nominal temperature had repetitive temperature histories.

The products were quantitatively recovered from the reactor and filtered under vacuum on a microfiber filter (Prat-Dumas, diameter 47 mm, thickness 0.27 mm, pore size 1.2 μm), attached to a tared 50 mL polypropylene centrifuge tube to collect the filtrate. To ensure quantitative recovery of the entire sample during filtration, the reactor and the retained solid were carefully washed with 30.0 mL of deionized water, which were collected with the liquid product. The solid fraction was dried at 105 ± 5 °C, weighed to calculate conversion, and analyzed for carbohydrates and lignin as described in section 2.3. An aliquot of 9.0 mL of the liquid was taken to be analyzed by HPLC for carbohydrate-derived products, also as described in section 2.3. About 4 g of solid sodium chloride was added to the liquid remaining in the centrifuge tube. It was then thoroughly mixed and let to rest to separate an organic phase and an aqueous phase, the first containing the solubilized lignin and the second most of the carbohydrates [15, 16, 18]. When the two phases were completely decanted the aqueous phase was removed with the aid of a syringe. Lignin was then precipitated from the organic phase by adding 50 mL of a sulfuric acid solution at pH 1, mixing, and subsequently centrifuging at 7500 rpm for 10 min; the liquid was then decanted and discharged. The precipitated lignin contained in the centrifuge tube was dried under full vacuum at room temperature until constant weight, and the yield of lignin calculated on the basis of the initial mass of almond shells applying the required sample dilution and splitting factors.

2.3 Analytical methods

Summative chemical analysis of the powdered almond shells was conducted according to the National Renewable Energy Laboratory (NREL) biomass compositional analysis laboratory methods. Moisture in biomass and solid samples was determined gravimetrically by drying at 105 ± 5 °C according to the NREL/TP-510-42621 procedure [23]. The content of inorganic materials in the native almond shells was determined by ashing at 575 ± 25 °C following the NREL/TP-510-42622 laboratory method [24]. Determination of water- and ethanol-soluble extractives were performed by successive extraction in a Soxhlet apparatus as specified in NREL/TP-510-42619 [25]. The content of Klason lignin, acid soluble lignin, the main constitutive monosaccharides forming cellulose and hemicellulose, as well as acetyl groups in the latter, were measured on extractive-free samples of almond shells following procedures adapted from the methods given in NREL/TP-510-42618 [26]. The same methods were used to analyze the hydrolyzed solid recovered from the reactor as well. Sample amounts equivalent to ca. 0.3 g of dry biomass were thoroughly mixed with 3.0 mL of 24 N sulfuric acid and kept in a water bath at 30 ± 2 °C for 1h. Then the samples were diluted with deionized water to an acid concentration of 0.84 N and further hydrolyzed at 120 ± 3 °C for 1h in an autoclave. Once cold, the samples were filtered under vacuum on tared microfiber filters. The

recovered solid was washed with hot water and dried at 105 ± 5 °C to quantify Klason lignin. Another aliquot of the liquid was taken to measure carbohydrates and acetyl groups by HPLC using an Agilent 1100 series instrument equipped with a refractive index (RI) detector. An Agilent HI-Plex H column was employed with a flowrate of 0.6 mL/min of 0.005 M H_2SO_4 acid as eluent, a column temperature of 65 °C, a sample injection volume of 50 μL, and a RI detector temperature of 40 °C. This column allowed a good separation of glucose, xylose, arabinose, acetic acid and furfural, but other constitutive monosaccharides such rhamnose, galactose and mannose were not resolved. However, these are minor in almond shells [20-22, 27] and their contribution to the total amount of hemicellulose is quite small. The HPLC peaks were identified by comparison of their retention time with standards prepared with pure (analytical grade) compounds, which were also used for calibration. Also, standard solutions were employed to quantify sugar degradation during the high temperature acid hydrolysis step in the autoclave [26]. Control samples with known concentrations of monosaccharides in 0.84 N sulfuric acid were placed in the autoclave together with the samples to be analyzed, and a recovery factor was calculated for each monosaccharide based on the decrease of concentration caused by the autoclave treatment.

Carbohydrates, acetic acid and furfural in the liquid product recovered from the reactor were also analyzed by HPLC based on the NREL/TP-510-42623 methods [28]. A sample of the liquid was filtered through a syringe filter (pore size 0.22 μm, Filter-Bio) and injected into the HPLC system to quantify the yields of monomeric products (glucose, xylose, arabinose, acetic acid and furfural) using the column and conditions already mentioned. Additional samples of 5.0 mL were adjusted to a 0.82 N sulfuric acid concentration and further hydrolyzed in an autoclave at 120 ± 3 °C for 1h to convert any possible oligosaccharides present in the solution – together with control solutions to determine the extent of monosaccharide degradation as explained above – and the products were analyzed by HPLC. The yield of oligosaccharides solubilized during a reaction was thus calculated from the difference in concentration between the hydrolyzed and non-hydrolyzed samples, after adjusting for the required dilution and sugar recovery factors.

All results of biomass composition and product yields were always reported based on 100 g of dry almond shells (%DSB), unless otherwise is stated explicitly.

3 Results and discussion

3.1 Composition of the almond shells

Summative analysis of almond shells gave the results shown in Table 1, where average values of triplicate analysis and their confidence intervals ($\alpha = 0.05$) are reported. The results agreed with those published in previous works for this type of biomass [20-22, 27]. The shells are the endocarp of the almond fruit and constitute a protective tissue. They consist of rounded stone cells with thick and highly lignified walls and small lumens, which explains the high content of lignin in this material (30.8 %DSB). The hemicellulose fraction (31.8 %DSB) consists essentially of arabinoxylan with arabinose/xylose and acetyl/xylose molar ratios of 0.016 and 0.175, respectively. Glucan content was 26.6 %DSB, and it could be assigned entirely to cellulose.

3.2 Almond shells conversion: effect of temperature

The effect of temperature was investigated in a series of experiments performed at a constant sulfuric acid concentration of 35 mM and a reaction time of 90 min, which included an initial heating period of ca. 30 min plus a nearly isothermal period of 60 min. Figure 2 shows the influence of reaction nominal temperature on the composition of the hydrolyzed solid and the products recovered in solution. The error bars depicted for the data at 140 °C correspond to the confidence intervals at a 95% probability level determined from a duplicate experiment and illustrate the uncertainties that may be expected from the experimental techniques used in this study (see also the scattering of duplicate and triplicate experiments in Figure 5). As seen in figure 2A, at 120 °C ca. 47 %DSB of the original biomass was converted into soluble products, while solubilization grew to 58 %DSB at 160 °C. Concerning the chemical composition of the hydrolyzed solid and the soluble products, cellulose – measured as anhydrous glucose by HPLC – was the polymer less susceptible to hydrolysis (figure 2B). Cellulose in solid decreased from 26.6 %DSB in the raw almond shells to 22.9 %DSB at 120 °C, and to 22.4 %DSB at 160 °C. The main product from cellulose hydrolysis was glucose and gluco-oligomers were only present in trace amounts regardless of temperature. The combined amounts of glucan recovered in the solid and the liquid tended to decrease with temperature which indicated that glucose was partially degraded to hydroxymethyl furfural (HMF) in the acidic GVL/water solution. Even if the presence of HMF in the solution could not be verified due to the interference of GVL in the HPLC analysis, trace amounts of formic and levulinic acids formed by the decomposition of HMF were detected.

Hemicellulose (figure 2C) and lignin (figure 2D) were more susceptible to hydrolysis than cellulose. The amounts of hemicellulose in the solid, which were calculated as the sum of anhydrous xylose, anhydrous arabinose and acetyl groups, fell from 31.8 %DSB in almond shells to 10.2 and 7.8 %DSB at 120 °C and 160 °C, respectively. Xylose was always the main product whit a maximum of 14.8 %DSB at 140 °C, but a significant fraction of soluble oligomers was also produced (5.4 at 120 °C and 5.1 %DSB at 160 °C). The amount of monosaccharides converted to furfural was only 0.12 %DSB at 120 °C but grew with temperature to 2.0 %DSB at 160 °C. Figure 3A compares the mass ratios between acetyl groups and anhydrous xylose and arabinose in the untreated almond shells with those remaining in the hydrolyzed solid, the soluble xylo-oligosaccharides, and the ratio between monomers (acetic acid to xylose plus arabinose). The ratio in the solid fell from 0.17 in almond shells to an average value of ca. 0.09 in the hydrolyzed solids, regardless of temperature. The ratio in the soluble oligomers, however, grew with temperature from 0.14 at 120 °C to 0.33 at 160 °C. This showed that xylo-oligosaccharides retained unhydrolyzed acetyl groups in their structure and also pointed to the presence of xylan fractions with different degree of acetylation in almond shells, the higher the acetyl content of the xylan fraction was, the easily it was solubilized in acidic GVL/water. Finally, the ratio between acetic acid and monosaccharides was close to that of the untreated almond shells.

Lignin conversion also grew with temperature (figure 2D). Lignin in the solid went from 30.3 %DSB in raw AS to 13.6 %DSB at 120 °C and 8.2 %DSB at 160 °C. The lignin precipitated from the liquid solution by salt addition, acidification and filtration (see section 2.2) was 11.8 %DSB at 120 °C but grew to 18.8 %DSB at 160 °C. Total recovery of lignin (i.e., combined amount of lignin remaining in the hydrolyzed shells and that recovered from the liquid) at 120 °C was significantly lower than

the lignin present in the raw biomass, and lower than the total recovery at higher temperature. This could be attributed to two phenomena. On the one hand, the oligomers produced by depolymerization of the native lignin at 120 °C might had a structure closer to that of native lignin and experience less recondensation reactions than those produced at higher temperature, thus being more soluble in the aqueous phases formed after adding NaCl to the GVL/water liquor and after acidification of the GVL phase. Meng et al. [29] reported that the use of GVL/water preserved a large fraction of the native β-O-4 linkages and most of the syringyl and guaiacyl groups in the lignin extracted from poplar wood at 120 °C, which also possessed a significant content of aliphatic OH groups and had a number of *p*-hydroxybenzoate end groups higher than that of the original lignin. On the other hand, the abundance of furfural together with the probable existence of HMF in acidic solution at high temperature would promote addition and condensation reactions, which would form humins that would precipitate upon addition of NaCl thus incrementing the yield of lignin compared to that at 120 °C. Formation of humins, commonly referred-to as pseudo-lignin, is a well-known phenomenon that has been reported in the autohydrolysis/steam-explosion pretreatment of biomass [22, 30, 31] and acetone organsolv fractionation [32], and has been investigated in detail in various solvents recently [33].

3.3 Almond shells conversion: effect of acid concentration

Figure 4 shows the influence of acid concentration on the composition of the hydrolyzed AS and the products recovered in solution for a group of reactions at 140 °C. Increasing the catalyst load promoted solubilization of almond shells, but the effect was less pronounced at concentrations above 35 mM. Solubilization grew from 30 %DSB at 25 mM sulfuric acid to 50 %DSB at 35 mM, but then went only to 54 %DSB at 75 mM (figure 4A). Cellulose in the solid decreased from 26.6 %DSB in the raw almond shells to 22.9 %DSB at 25 mM and to 19.5 %DSB at 75 mM, as observed in Figure 4B. Glucose was the main product an few gluco-oligomers were obtained. However, at 75 mM only trace amounts of gluco-oligomers and free glucose could be quantified, which suggested that glucose was readily degraded to hydroxymethyl furfural (HMF) at that acid concentration.

The yields of products derived from hemicellulose (figure 4C) were strongly dependent on acid concentration. At 25 mM hemicellulose in the solid decreased from 31.8 to 19.6 %DSB to yield 8.4 %DSB of xylo-oligomers, 3.1 %DSB of xylose and trace amounts of furfural. An acid concentration of 35 mM decreased hemicellulose in the solid to 9.5 %DSB but xylose (12.3 %DSB) was the main product followed by xylo-oligosaccharides (4.9 %DSB) and furfural (1.6 %DSB). Further increasing of the acid concentration had lower impact, but still promoted the removal of hemicellulose from the solid and the formation of xylose as the main product. However, at 75 mM a significant fraction of hemicellulose was lost to degradation products through furfural formation and polymerization, which increased the recovery of lignin as discussed below. The mass ratios between acetyl groups and anhydrous xylose and arabinose in the solid and the soluble products, shown in figure 3B, were dependent on acid concentration. The ratio in the hydrolyzed solid decreased gradually from 0.17 in the raw material to 0.09 at 45 mM and 0.75 mM. The ratio in the xylo-oligosaccharides tended to decrease with acid concentration and it was close to zero at 75 mM, pointing to a complete deacetylation. However, the ratio between acetic acid and monosaccharides was almost constant and close to that in the raw material. Concerning lignin, see figure 4D, acid concentrations above 35

mM did not improve solubilization significantly and the only observable effect was a higher recovery of precipitated lignin at 75 mM, which was probably caused by the inclusion of humins formed by the degradation of carbohydrates.

3.4 Almond shells conversion: effect of reaction time.

The influence of reaction time was explored at each combination of nominal temperature (120, 140 and 160 °C) and sulfuric acid concentration (25, 35, 45 and 50 mM), using four different reaction times, typically 15, 35, 45 and 90 min. Figure 5 shows the results obtained at 140 °C and 35 mM, which suffice to discuss the evolution of the composition of almond shells and the hydrolysis products. The profile of reactor temperature of one extended experiment is also shown in Figure 5B. Recall that the reaction time comprised both the period of reactor heating from the room temperature to the nominal temperature, plus the quasi-isothermal period once that was reached. Therefore, in the experiments shorter than ca. 30 min temperature was still well below the nominal value. As already discussed, cellulose was resilient to hydrolysis in acidic GVL/water and its rate of conversion was quite low. Only trace amounts of soluble gluco-oligomers were detected, showing that they were readily hydrolyzed to glucose. The concentration of the latter, however, reached a plateau value of ca. 2 %DSB, which meant that it was converted to HMF.

Hemicellulose followed a different trend. It was hydrolyzed and readily extracted during an initial period of 35 min and formed xylose together with significant amounts of xylo-oligosaccharides. This high reactivity period took place while the reactor was being heated, and therefore most conversion occurred under non-isothermal conditions. This was consistent with the findings of Mellmer et al. [10], who reported that operation with GVL/water mixtures leaded to higher rates of acid-catalyzed reactions at low temperature compared to reactions in water. After 50 min of reaction the rate of hemicellulose hydrolysis was substantially reduced, the yield of xylose tended to stabilize, that of xylo-oligosaccharides to decrease, and furfural production to increase showing that the rate of xylose dehydration outpaced its rate of formation from the xylo-oligosaccharides. Analysis of the acetyl-to-monosaccharides (xylose plus arabinose) ratio revealed that during the initial period the ratio in the unconverted hemicellulose and in the soluble monomers were constant and equal to that of the untreated AS. Noticeably however, the ratio in the xylo-oligosaccharides tended to increase, which would suggest that the rate of deacetylation of the xylo-oligosaccharides was lower than the rate of scission of the β-1,4 glycosidic bonds in the backbone of the oligosaccharides. At 90 min the ratio in the soluble monomers increased due to the consumption of pentoses to form furfural. Also, the ratio in the solid decreased below the value in the raw AS, which suggests that the more resilient hemicellulose that still remained in the solid had a lower degree of acetylation than the hemicellulose that was extracted during the initial stages of the reaction.

Lignin conversion followed the same pattern than hemicellulose. During the heating period lignin was easily hydrolyzed but after 50 min the amount of lignin in the hydrolyzed solid reached a nearly constant value of ca. 12 %DSB. The yield of high molar mass lignin recovered by precipitation from the GVL/water solution grew also rapidly during the heating period and remained nearly constant afterwards at ca. 15%. However, the latter probably included products formed by condensation of furfural and HMF. Experiments performed at other acid concentrations and

temperatures followed the same qualitative trends. Cellulose conversion and yield of glucose were always low. The amount of lignin and hemicellulose in the hydrolyzed biomass evolved with time starting with a period of fast conversion, which roughly corresponded to the interval of reactor heating, followed by the approach towards an asymptotic value as reaction time was extended. Hemicellulose formed monomers and xylo-oligomers, with furfural production growing faster in the longest experiments.

4 Kinetics of hemicellulose and lignin solubilization

Separation and recovery of hemicellulose, lignin and cellulose are critical to profitability in any biorefinery concept, where the valorization of the entire biomass feedstock into a few marketable products must be achieved. The technoeconomic analysis and optimization of biorefineries require of detailed models to simulate the process units. Among those, kinetic models capable of describing biomass conversion under changing process conditions are needed to optimize the fractionation reactors. Rigorous mechanistic modeling of biomass processing in aqueous and organoslov media is a formidable task because of the inherent heterogeneity of biomass and the complex relationship between its constitutive polymers in the vegetable cell wall. This is why simplified kinetic models based on pseudo-homogeneous reactions have been usually adopted to describe biomass fractionation with reasonable accuracy, and this is the approach we have followed for AS fractionation in GVL/water as well.

4.1 Model development

The kinetics of hydrolytic treatments of biomass for the extraction of hemicellulose or delignification in a variety of solvents and catalysts has been modeled following several approaches since Seaman introduced its model for the dilute acid hydrolysis of cellulose at high temperature [34]. A common feature in most models is to consider that the polymer under study is not homogeneous but is assumed to be formed for at least two fractions that react in parallel at different rate. Among others, models based on this core idea have applied to several studies on biomass fractionation in aqueous media [35- 37] and organosolv processes [38-44]. The same approach was adopted in the kinetic model proposed here to describe the hydrolysis and solubilization of hemicellulose and lignin in acidic GVL/water. The model assumed that each polymer consisted of three fractions with different reactivity: fast-reacting, slow-reacting and unreactive. The existence of such fractions was attributed to a high association of hemicellulose and lignin with cellulose in some locations of the cell wall structure, which had lower porosity and were less accessible to hydrolytic attack. However, the susceptibility of lignin and hemicellulose to dilute acid hydrolysis should also depend on the capacity of the solvent to swell the cell wall structure and solvate and extract the high molar mass oligomers produced in the first stages of hydrolysis. Besides the chemical properties of the solvent this capacity should also be influenced by parameters such as temperature and acidity. Two versions of the model were therefore tested. Model-I assumed constant amounts of the three fractions of each polymer, while in model-II those amounts were correlated with acid concentration and temperature. The use of fractions with different reactivity whose amounts depended on process

conditions was introduced recently to describe the kinetics of bamboo delignification in an autocatalyzed ethanol organosolv process, where the amounts of reactive and unreactive lignin were correlated with temperature and the concentration of ethanol in the pulping liquor [35].

Given the total content of a polymer in native biomass (c_p^0), expressed as mass percentage of the original AS on a dry basis (%DSB), the amount of each fraction ($c_{p,l}^0$) is calculated with equation 1, where subscript p denotes the polymer, either lignin (L) or hemicellulose (H), subscript l identifies the type of fraction – fast-reacting (f), slow-reacting (s) and unreactive (u) – and $w_{p,l}$ is the unit mass fraction of each type, which fulfill the restriction given in equation 2.

$$c_{p,l}^0 = c_p^0 w_{p,l} \quad [1]$$

$$\sum_{l=f,s,u} w_{p,l} = 1 \quad [2]$$

Assuming first order dependencies of the rates of hydrolysis of each fraction with their respective content in biomass and the concentration of sulfuric acid in the solvent, c_A, the rates of solubilization of each fraction and the total amount of polymer remaining in the solid are given by equations 3 and 4, respectively. The rate constants, $k_{p,l}$, were assumed to follow an Arrhenius dependency with temperature, expressed in the reparametrized form given by equation 5 to reduce the correlation between activation energy and preexponential factor. A reference temperature T^0 of 413.15 K was used in the calculations.

$$\frac{dc_{p,l}}{dt} = -k_{p,l} c_{p,l} c_A \quad [3]$$

$$c_p = \sum_{l=f,s,u} c_{p,l} \quad [4]$$

$$k_{p,l} = k_{p,l}^0 \exp\left(-\frac{E_{p,l}}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right) \quad [5]$$

Concerning model-II, the amounts of unreactive and slow reacting fractions of hemicellulose and lignin were correlated with the final reactor temperature of each non-isothermal experiment, T_∞, and its acid concentration according to equations 6 and 7, while the amount of the fast-reacting fraction was calculated by difference.

$$w_{p,s} = 1 - \frac{a_0}{T_\infty} - a_1 c_A \quad [6]$$

$$w_{p,u} = 1 - \frac{a_2}{T_\infty} - a_3 c_A \quad [7]$$

$$w_{p,f} = 1 - w_{p,s} - w_{p,u} \quad [8]$$

To describe the conversion of the p^{th} polymer (either hemicellulose or lignin), model-I required a total of six unknown parameters, the activation energies ($E_{p,f}$, $E_{p,s}$), the rate constants at the base temperature ($k_{p,f}^0$, $k_{p,s}^0$), and the fractional amounts of fast- and slow-reacting fractions

($w_{p,f}$, $w_{p,s}$). The fractional amount of unreactive polymer ($w_{p,u}$) was obtained from the restriction in equation 2, and the rate constant for the unreactive fraction ($k_{p,u}$) was set to zero. Similarly, model-II had a total of eight parameters; the activation energies, rate constants at the base temperature, and the four constants involved in equations 6 and 7 (a_0, a_1, a_2 and a_3). The values of those parameters were estimated separately for hemicellulose and lignin by a least squares minimization of the objective function given in equation 9, where p and l are the subscripts defined above, n_A is the number of levels of acid concentration tested (25, 35, 45 and 50 mM), $n_{T(i)}$ is the number of nominal temperature levels tested at each value of acid concentration (120, 140 and 160 °C), $n_{t(i,j)}$ is the number of experiments at different reaction times performed at each combination of nominal temperature and acid concentration, and $c'_p(i,j,k)$ are the experimental values of polymer remaining in the hydrolyzed solid measured in each experiment, expressed as percentage of the original AS on a dry basis (%DSB). The model predictions of each fraction of polymer in the solid, $c_{p,l}(i,j,k)$, were obtained by numerical integration of equation 3 for the fast- and slow-reacting fractions imposing the values from equation 1 as initial conditions. The temperature register of each non-isothermal experiment was used to perform the integration. Minimization of the objective function was conducted with Matlab R2019b (MathWorks) using the *fminsearch* function.

$$OF_p = \sum_{i=1}^{n_A} \sum_{j=1}^{n_{T(i)}} \frac{1}{n_{t(i,j)}} \sum_{k=1}^{n_{t(i,j)}} \left(1 - \frac{1}{c'_p(i,j,k)} \sum_{l=f,s,u} c_{p,l}(i,j,k) \right)^2 \quad [9]$$

4.2 Results of the kinetic modelling

Table 2 shows the best-fit values of the parameters in models I and II for the hydrolysis of hemicellulose and lignin. The values of activation energies for the fast- and slow-reacting fractions of hemicellulose in model-I were 118. and 52.0 kJ mol^{-1}, which are in the low tier of the values usually reported in literature for the acid hydrolysis of hemicellulose in aqueous media [36, 37], but similar to those of acid-catalyzed ethanol organosolv pulping [39, 41]. Activation energies for lignin (106. and 58.7 kJ mol^{-1} for the fast and slow fractions) were similar to those reported for acid-catalyzed organosolv pulping in ethanol [38, 39, 41], but higher than those in soda-ethanol delignification [43], aqueous p-toluene sulfonic acid pulping [44], and aqueous acetic acid pulping [40]. The predicted fractions of non-reacting polymers were 0.119 and 0.226 for hemicellulose and lignin, respectively, while the slow-reacting fractions were 0.386 and 0.383. Figure 6 compares the experimental evolution of hemicellulose and lignin in the hydrolyzed almond shells at 50 mM sulfuric acid and 120, 140 and 160 °C with the predictions of model-I using the best-fit values in Table 2. Overall, the model predicted the trend of a fast rate of conversion during the initial stage of the reaction, followed by a period of lower reactivity. Agreement with experimental data was reasonably good for both lignin and hemicellulose at 120 °C but at higher temperature the model underpredicted the extent of conversion. Figure 7 shows the entire set of experimental data and model-I predictions. A large dispersion was obtained, especially at 25 mM of acid where the model underpredicted the degree of conversion of lignin and, even more clearly, that of hemicellulose.

Model-II provided a better description of the evolution of lignin and hemicellulose along reaction time. Figure 6 shows a reasonable agreement with experimental data at 120, 140 and 160

°C. Comparison of model-II with the entire set of data in Figure 7 shows a better agreement than with model-I. Although scattering was still significant, it was randomly distributed and could be explained, at least partially, considering the dispersion of the experimental data. The activation energies in model-II were 142. and 39.7 kJ mol^{-1} for the fast- and slow-reacting hemicellulose, respectively, which are still lower than in aqueous-phase hydrolysis, especially for the slow-reacting fraction [36, 37]. The reduction in the activation energy in the acid-catalyzed hydrolysis of saccharides in GVL/water mixtures when compared to reactions in water was attributed to the influence of GVL on stabilizing the acidic proton relative to the protonated transition states [45]. Concerning lignin, activation energy was 134. for the fast-reacting and 71.7 kJ mol^{-1} for the slow-reacting fractions. The values of the parameters in equations 6 and 7 showed that acid concentration had a larger influence than temperature on establishing the amounts of slow-reacting hemicellulose and lignin, whereas temperature was the dominant process variable concerning the fractions of non-reacting polymers, which in the case of hemicellulose was practically independent of acid concentration.

5 Conclusions

The effectiveness of the acid-catalyzed fractionation of almond shells in GVL/water at a constant mass ratio of 80% w/w GVL was assessed at nominal temperatures from 120 to 160 °C and sulfuric acid concentrations from 25 to 75 mM. The addition of GVL resulted on high rates of solubilization of lignin and hemicellulose, even at low temperature. In fact, due to the moderate heating rates that were intrinsic to the reactors that were used, most solubilization took place during the heating period and conversion grew only marginally after the target temperature was attained. A temperature of 140 °C gave slightly better yields of soluble hemicellulose saccharides and less furfural formation than 160 °C. However, the latter was better than 140 °C regarding the amount of lignin extracted from almond shells and recovered from the pulping liquor by precipitation. Sulfuric acid concentration was also a key parameter. Hemicellulose recovery increased with acid concentration up to 50 mM, but degradation to furfural and its condensation products accelerated at higher concentrations, thus decreasing yield. However, cellulose degradation, albeit moderate, started to grow above 45 mM. Lignin removal grew continuously with acid concentration, and 75 mM gave the highest delignification of the almond shells and the higher yields of lignin recovered by precipitation, but cellulose degradation was significant. Overall, a compromise in temperature and acid concentration has to be reached to obtain enough delignification and prevent excessive degradation of cellulose and, specially, hemicellulose. Kinetics of lignin and hemicellulose solubilization were described with a model that included three fractions of different reactivity for each polymer. Better results were obtained when the amount of each fraction was assumed to be not constant, but dependent on acid concentration and the final temperature of the reaction.

6 References

1. Bozell JJ, Petersen GR (2010) Technology development for the production of biobased products from biorefinery carbohydrates - the US Department of Energy's "Top 10" revisited. Green Chem 12:539–554. https://doi.org/10.1039/b922014c
2. Bodachivskyi I, Kuzhiumparambil U, Williams DBG (2018) Acid-Catalyzed Conversion of Carbohydrates into Value- Added Small Molecules in Aqueous Media and Ionic Liquids. ChemSusChem 11:642-660. https://doi.org/10.1002/cssc.201702016
3. Sun Z, Fridrich B, de Santi A, Elangovan S, Barta K (2018) Bright Side of Lignin Depolymerization: Toward New Platform Chemicals. Chem Rev 118:614−678. https://doi.org/10.1021/acs.chemrev.7b00588
4. Paone E, Tabanelli T, Mauriello F (2020) The rise of lignin biorefinery. Curr Opin Green Sustainable Chem 24:1-6. https://doi.org/10.1016/j.cogsc.2019.11.004
5. Agbor VB, Cicek N, Sparling R, Berlin A, Levin DB (2011) Biomass pretreatment: fundamentals toward application. Biotechnol Adv 29:675–685. https://doi.org/10.1016/j.biotechadv.2011.05.005
6. Kumar AK, Sharma S (2017) Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. Bioresour Bioprocess 4:7. https://doi.org/10.1186/s40643-017-0137-9
7. Zhao X, Cheng K, Liu D (2009) Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. Appl Microbiol Biotechnol 82:815–827. https://doi.org/10.1007/s00253-009-1883-1
8. Zhao X, Li S, R Wu, Liu D (2017) Organosolv fractionating pre-treatment of lignocellulosic biomass for efficient enzymatic saccharification: chemistry, kinetics, and substrate structures. Biofuels, Bioprod Bioref 11:567–590. https://doi.org/10.1002/bbb.1768
9. Zhang Z, Harrison MD, Rackemann DW, Doherty WOS, O'Hara IM. Organosolv pretreatment of plant biomass for enhanced enzymatic saccharification. Green Chem 18: 360-381. https://doi.org/ 10.1039/c5gc02034d
10. Mellmer MA, Alonso DM, Luterbacher JS, Galloa JMR, Dumesic JA (2014) Effects of γ-valerolactone in hydrolysis of lignocellulosic biomass to monosaccharides. Green Chem 16:4659–4662. https://doi.org/10.1039/C4GC01768D
11. Le HQ, Ma Y, Borrega M, Sixta H (2016) Wood biorefinery based on γ-valerolactone/water fractionation. Green Chem 18:5466–5476. https://doi.org/10.1039/C6GC01692H
12. Fang W, Sixta H (2015) Advanced Biorefinery based on the Fractionation of Biomass in γ-Valerolactone and Water. ChemSusChem 8: 73–76. https://doi.org/10.1002/cssc.201402821
13. Zhang L, Zhen W, Wang Z, Maa Y, Jiang L, Wang T (2018) Efficient degradation of lignin in raw wood via pre-treatment with heteropoly acids in γ-valerolactone/water. Bioresour Technol 261:70–75. https://doi.org/10.1016/j.biortech.2018.03.141
14. Shuai L, Questell-Santiago YM, Luterbacher JS (2016) A mild biomass pre-treatment using γ-valerolactone for concentrated sugar production. Green Chem 18:937–943. https://doi.org/10.1039/C5GC02489G
15. Trevorah RM, Huynh T, Vancov T, Othman MZ (2018) Bioethanol potential of Eucalyptus Obliqua sawdust using gamma-valerolactone fractionation. Bioresour Technol 250:673–682. https://doi.org/10.1016/j.biortech.2017.11.084

16. Zhou X, Ding D, You T, Zhang X, Takabe K, Xu F (2018) Synergetic dissolution of branched xylan and lignin opens the way for ezymatic hydrolysis of Poplar cell wall. J Agric Food Chem 66:3449−3456. https://doi.org/10.1021/acs.jafc.8b00320
17. Qing Q, Gao X, Wang P, Guo Q, Xu Z, Wang L (2018) Dilute acid catalyzed fractionation and sugar production from bamboo shoot shell in γ-valerolactone/water medium. RSC Adv. 8:17527–17534. https://doi.org/10.1039/C8RA02891E
18. Li S, Li M, Yu P, Fan Y, Shou J, Sun R (2017) Valorization of bamboo by γ-valerolactone/acid/water to produce digestible cellulose, degraded sugars and lignin. Bioresour Technol 230:90–96. https://doi.org/10.1016/j.biortech.2017.01.041
19. Wu M, Yan ZY, Zhang XM, Xu F, Sun RC (2016) Integration of mild acid hydrolysis in γ-valerolactone/water system for enhancement of enzymatic saccharification from cotton stalk. Bioresour Technol 200:23-28. https://doi.org/10.1016/j.biortech.2015.09.111
20. Queirós CSGP, Cardoso S, Lourenço A, Ferreira J, Miranda I, Lourenço MJV, Pereira H. (2020) Characterization of walnut, almond, and pine nut shells regarding chemical composition and extract composition. Biomass Conv Bioref 10:175–188. https://doi.org/10.1007/s13399-019-00424-2
21. Montané D, Salvadó J, Farriol X, Chornet E (1993) The fractionation of almond shells by thermomechanical aqueous phase (TMAV) pretreatment. Biomass Bioenergy 4:427–437. https://doi.org/10.1016/0961-9534(93)90064-B
22. Martínez JM, Granado JM, Montané D, Salvadó J, Farriol X (1995) Fractionation of residual lignocellulosics by dilute-acid prehydrolysis and alkaline extraction: application to almond shells. Bioresour Technol 52:59–67. https://doi.org/10.1016/0960-8524(95)00005-Y
23. Sluiter A, Hames B, Hyman D, Payne C, Ruiz R, Scarlata C, Sluiter J, Templeton D, Wolfe J (2008) Determination of total solids in biomass and total dissolved solids in liquid process samples. Technical Report NREL/TP-510-42621
24. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D (2005) Determination of ash in biomass. Technical Report NREL/TP-510-42622
25. Sluiter A, Ruiz R, Scarlata C, Sluiter J, Templeton D (2005) Determination of extractives in biomass. Technical Report NREL/TP-510-42619
26. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, Crocker D (2012) Determination of structural carbohydrates and lignin in biomass. Technical Report NREL/TP-510-42618
27. Nabarlatz D, Montané D, Kardošová A, Bekešová S, Hríbalová V, Ebringerová A (2007) Almond shell xylo-oligosaccharides exhibiting immunostimulatory activity. Carbohydr Res 342:1122–1128. https://doi.org/10.1016/j.carres.2007.02.017
28. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D (2006) Determination of sugars, byproducts, and degradation products in liquid fraction process samples. Technical Report NREL/TP-510-42623
29. Meng X, Bhagia S, Wang Y, Zhou Y, Pu Y, Dunlap JR, Shuai L, Ragauskas AJ, Yoo CG (2020) Effects of the advanced organosolv pretreatment strategies on structural properties of woody biomass. Ind Crops Prod 146:112114. https://doi.org/10.1016/j.indcrop.2020.112144
30. Overend R, Chornet E (1987) Fractionation of lignocellulosics by steam-aqueous pretreatments. Phil Trans Royal Soc London A321:523–536. https://doi.org/10.1098/rsta.1987.0029

31. Heitz M, Capek-Ménard E, Koeberle PG, Gagné J, Chornet E (1991). Fractionation of Populus tremuloides at the pilot plant scale: optimization of steam pretreatment conditions using the STAKE II technology. Bioresour Technol 35:23–32. https://doi.org/10.1016/0960-8524(91)90078-X
32. Smit A, Huijgen W (2017) Effective fractionation of lignocellulose in herbaceous biomass and hardwood using a mild acetone organosolv process. Green Chem 19:5505–5514. https://doi.org/10.1039/C7GC02379K
33. Shi N, Liu Q, Cen H, Ju R, He X, Ma L (2020) Formation of humins during degradation of carbohydrates and furfural derivatives in various solvents. Biomass Convers Biorefin 10:277–287. https://doi.org/10.1007/s13399-019-00414-4
34. Saeman JF (1945) Kinetics of wood saccharification-hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature. Ind Eng Chem 37: 43−52. https://doi.org/10.1021/ie50421a009
35. Nabarlatz D, Farriol X, Montané D (2004) Kinetic modeling of the autohydrolysis of lignocellulosic biomass for the production of hemicellulose-derived oligosaccharides. Ind Eng Chem Res 43: 4124-4131. https://doi.org/10.1021/ie034238i
36. Jensen J, Morinelly J, Anglan A, Mix A, Shonnard DR (2008) Kinetic characterization of biomass dilute sulfuric acid hydrolysis: mixtures of hardwoods, softwood, and switchgrass. AIChE J 54:1637-1645. https://doi.org/10.1002/aic.11467
37. Shi S, Guan W, Kang L, Lee YY (2017) Reaction kinetic model of dilute acid-catalyzed hemicellulose hydrolysis of corn stover under high-solid conditions. Ind Eng Chem Res 56:10990-10997. https://doi.org/10.1021/acs.iecr.7b01768
38. Oliet M, Rodríguez F, Santos A, Gilarranz MA, García-Ochoa F, Tijero J (2000) Organosolv delignification of eucalyptus globulus: kinetic study of autocatalyzed ethanol pulping. Ind Eng Chem Res 39:34-39. https://doi.org/ 10.1021/ie9905005
39. Sidiras D, Koukios E (2004) Simulation of acid-catalysed organosolv fractionation of wheat straw. Bioresour Technol 94:91-98. https://doi.org/10.1016/j.biortech.2003.10.029
40. Zhao X, Liu D (2013) Kinetic Modeling and Mechanisms of Acid-Catalyzed Delignification of Sugarcane Bagasse by Aqueous Acetic Acid. Bioener Res 6:436-447. https://doi.org/10.1007/s12155-012-9265-4
41. Sharazi AM, Van Heiningen A (2017) Kinetics of sulfur dioxide-alcohol-water (SAW) pulping of sugarcane straw (SCS). Tappi J 16:313-328.
42. Liu J, Gong Z, Yang G, Chen L, Huang L, Zhou Y, Luo X (2018) Novel kinetic models of xylan dissolution and degradation during ethanol based auto-catalyzed organosolv pretreatment of bamboo. Polymers 10:1449. https://doi.org/10.3390/polym10101149
43. Dagnino EP, Felissia FE, Chamorro E, Area MC (2018) Studies on lignin extraction from rice husk by a soda-ethanol treatment: Kinetics, separation, and characterization of products. Chem Eng Res Des 129:209-216. https://doi.org/10.1016/j.cherd.2017.10.026
44. Duan Q, Shuai X, Yang D, Zhou X, Gao T (2020) Kinetic analysis of pulping of rice straw with p-toluene sulfonic acid. ACS Omega 5:7787-7791. https://dx.doi.org/10.1021/acsomega.9b03622
45. Mellmer MA, Sener C, Gallo JMR, Luterbacher JS, Alonso DM, Dumesic JA (2014) Solvent effects in acid-catalyzed biomass conversion reactions. Angew Chem Int Ed 53:11872–11875. https://doi.org/10.1002/anie.201408359

Table 1 Summative chemical composition of almond shells on dry basis

Composition (%DSB)	Mean	Confidence interval (α = 0.05)
Ash	1.7	0.1
Water extractives	5.5	0.1
Ethanol extractives	0.3	0.2
Lignin	30.3	0.4
Glucan	26.6	0.6
Xylan	26.7	0.2
Arabinan	0.43	0.05
Acetyl	4.68	0.05

Table 2 Best fit values of the parameters of kinetic models I and II for hemicellulose and lignin hydrolysis in acidic GVL/water (80/20).

	Model-I		Model-II	
Parameter	Hemicellulose	Lignin	Hemicellulose	Lignin
$E_f\ (kJ\ mol^{-1})$	118.	106.	142.	134.
$E_s\ (kJ\ mol^{-1})$	52.0	58.7	39.7	71.7
$k_f^0 (L\ mol^{-1} min^{-1})$	9.472	3.895	11.1	5.39
$k_s^0 (L\ mol^{-1} min^{-1})$	0.351	0.302	0.240	0.213
$w_s\ (-)$	0.386	0.383	-	-
$w_u\ (-)$	0.119	0.226	-	-
$a_0\ (K^{-1})$	-	-	$2.26\ 10^{-4}$	$6.40\ 10^{-4}$
$a_1\ (L\ mol^{-1})$	-	-	14.8	11.1
$a_2\ (K^{-1})$	-	-	$2.06\ 10^{-3}$	$1.55\ 10^{-3}$
$a_3\ (L\ mol^{-1})$	-	-	$3.69\ 10^{-3}$	1.55
OF residual value	0.507	0.285	0.230	0.182

Figure captions

Figure 1 Reproducibility of the temperature profile during the heating period of three experiments performed at a nominal temperature of 120 °C and different reaction durations

Figure 2 Effect of temperature on the conversion of almond shells at 35 mM sulfuric acid and 90 min. **A)** cellulose ☐, lignin ☐, hemicellulose ☐, extractives ☐, ash ■. **B)** cellulose ☐, soluble gluco-oligomers ☐, glucose ☐. **C)** hemicellulose ☐, soluble xylo-oligomers ☐, xylose + arabinose ☐, furfural ☐. **D)** lignin in solid ☐, lignin recovered from liquid ☐

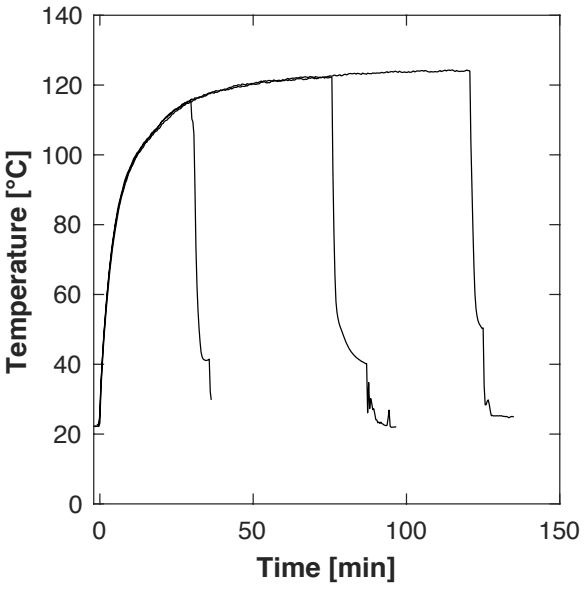
Figure 3 Effect of temperature at 35 mM sulfuric acid (left), and acid concentration at 140 °C (right), on the mass ratio between acetyl groups and xylan (xylose + arabinose) at 90 min of reaction: hydrolyzed solid ○, soluble oligomers △, monomers (acetic acid to monosaccharides) ☐. The continuous horizontal line is the ratio in the unprocessed almond shells; dashed lines only indicate trends

Figure 4 Effect of sulfuric acid concentration on the conversion of almond shells at 140 °C and 90 min. **A)** cellulose ☐, lignin ☐, hemicellulose ☐, extractives ☐, ash ■. **B)** cellulose ☐, soluble gluco-oligomers ☐, glucose ☐. **C)** hemicellulose ☐, soluble xylo-oligomers ☐, xylose + arabinose ☐, furfural ☐. **D)** lignin in solid ☐, lignin recovered from liquid ☐

Figure 5 Effect of reaction time on the conversion of almond shells at 35 mM of sulfuric acid and a nominal temperature of 140 °C. **A)** Cellulose ○, gluco-oligomers △, glucose ☐. **B)** Lignin in the hydrolyzed solid ○, lignin recovered by precipitation △. **C)** Hemicellulose in the hydrolyzed solid ○, xylo-oligomers △, xylose + arabinose ☐, furfural ■. **D)** Mass ratio between acetyl groups and xylan (xylose + arabinose) in the solid ○, xylo-oligomers △, monomers ☐. The continuous line in panel **B** shows the typical reactor temperature profile at 140 °C. The dashed lines only indicate trends

Figure 6 Evolution of lignin (top) and hemicellulose (bottom) remaining in the hydrolyzed AS (%DSB). Comparison between the experimental values and the predictions of the kinetic models I (left) and II (right) at 50 mM sulfuric acid at 120 °C ○, 140 °C △, and 160 °C ☐

Figure 7 Lignin (top) and hemicellulose (bottom) remaining in the hydrolyzed AS (%DSB). Comparison between the experimental values and the predictions of the kinetic models I (left) and II (right). Temperature: white symbols 120 °C, gray symbols 140 °C, black symbols 160 °C. Sulfuric acid concentration: 25 mM ◇, 35 mM ○, 45 mM △, 50 mM ☐


Temperature [°C]
Time [min]
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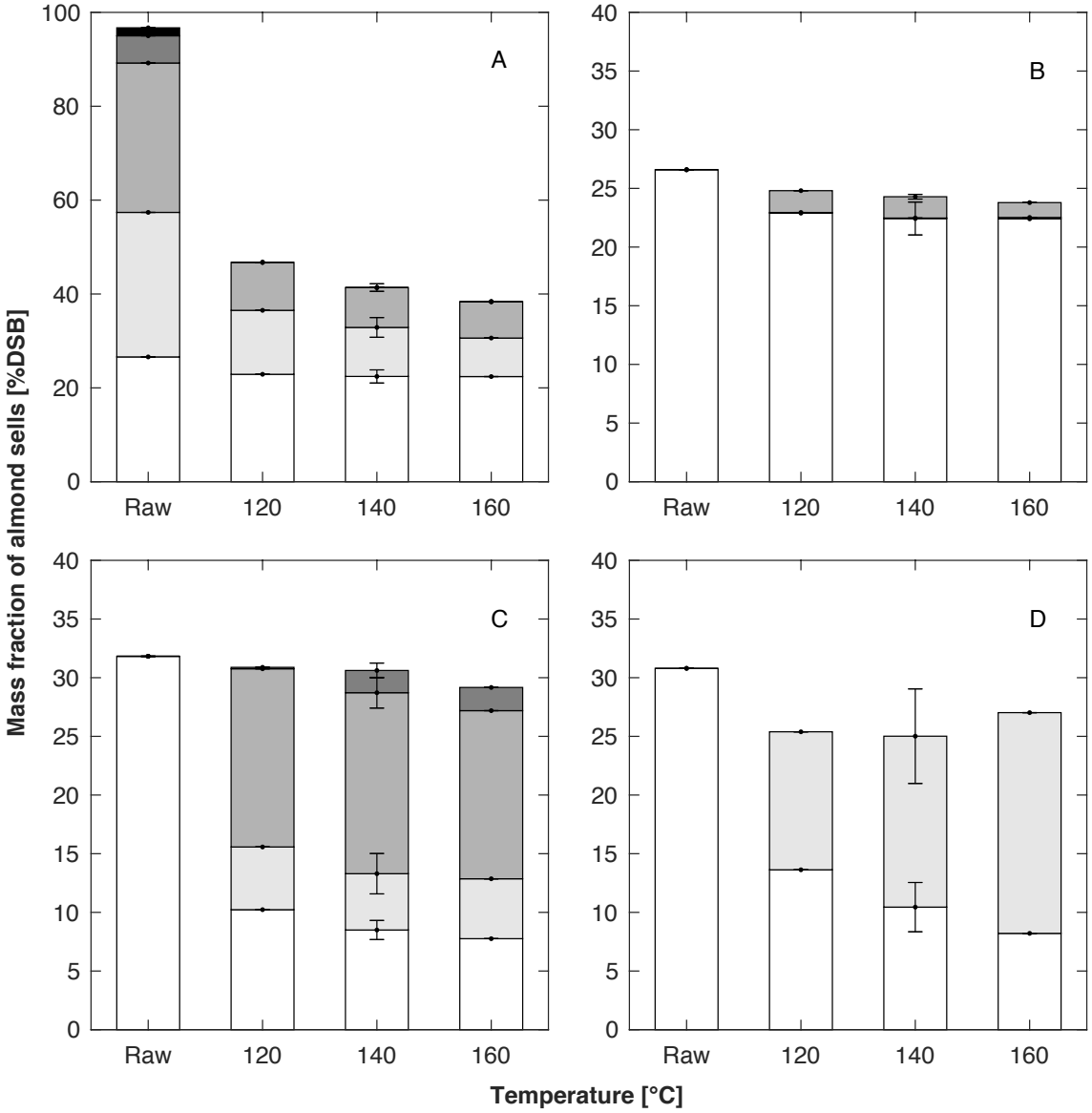
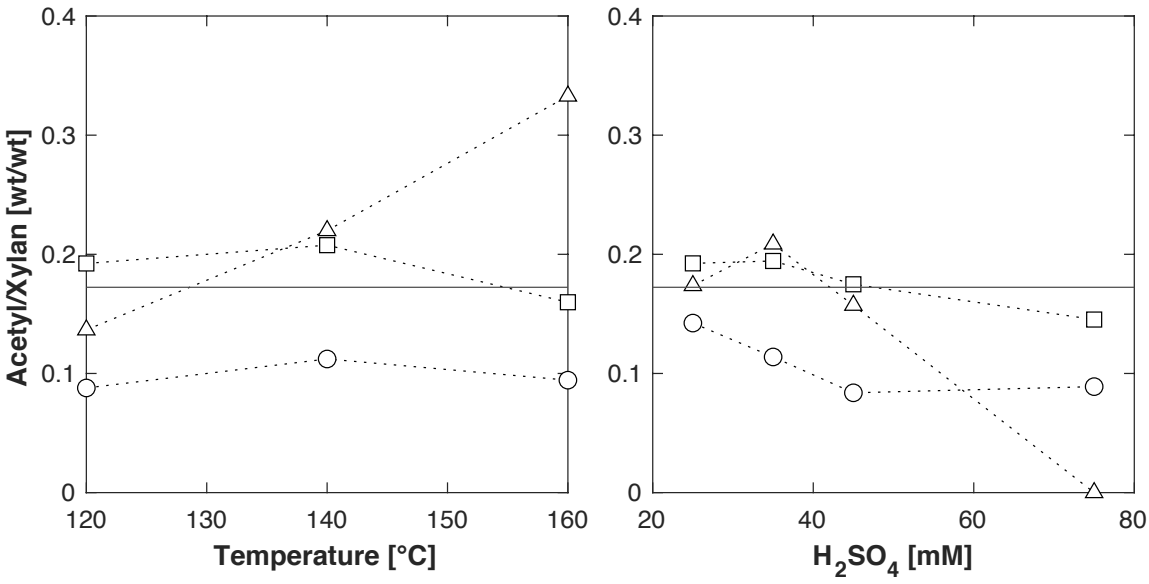
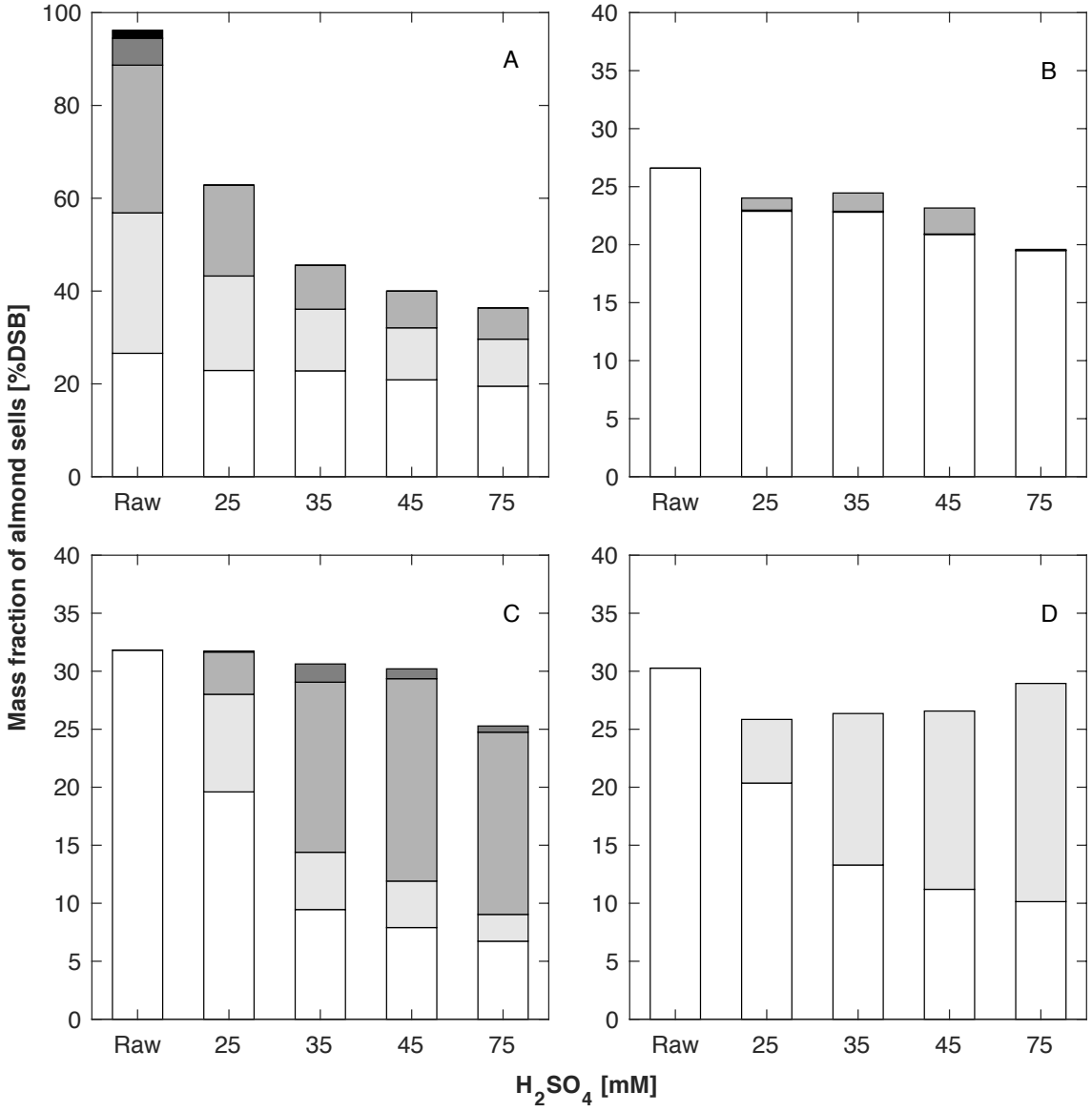
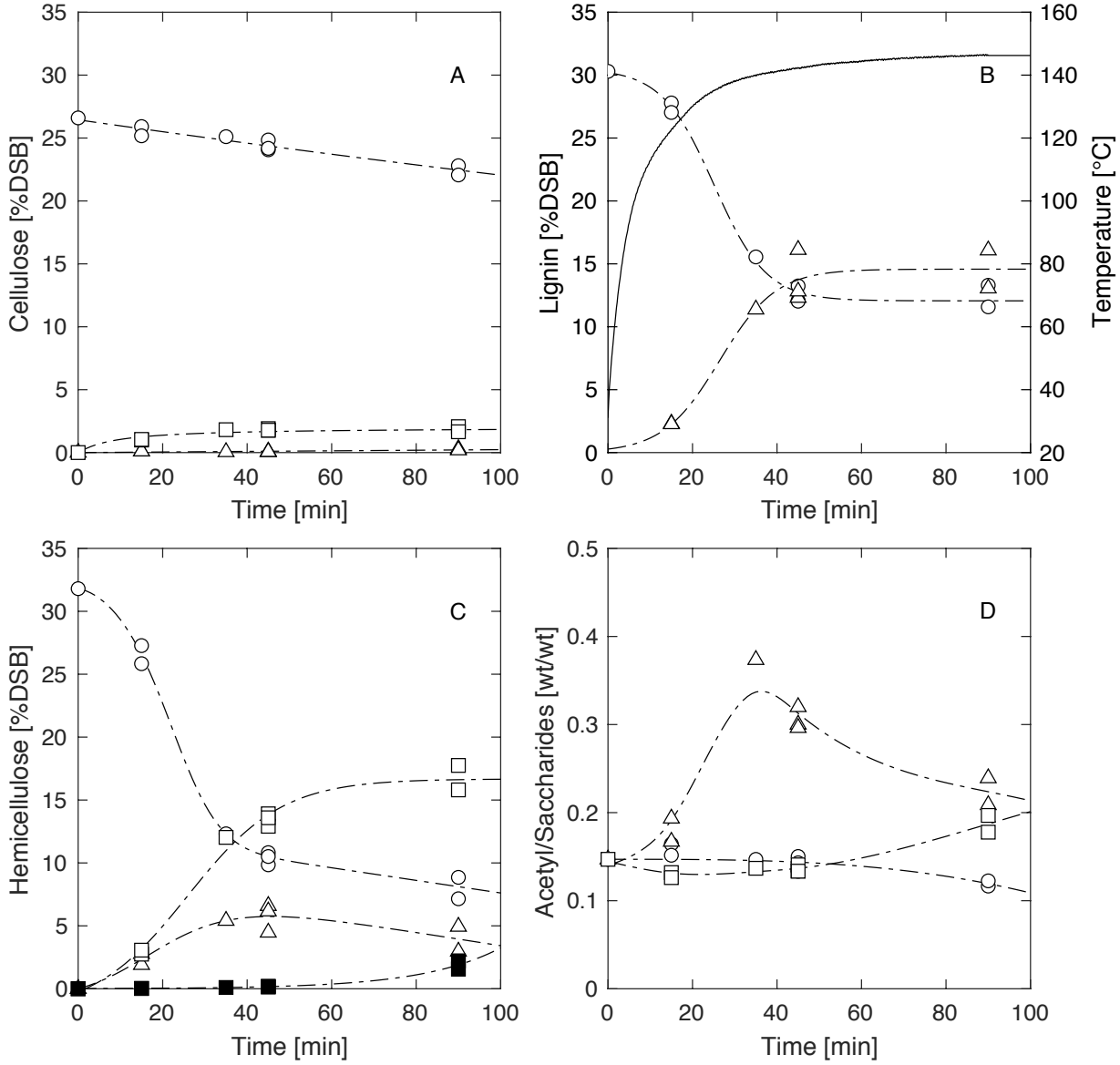
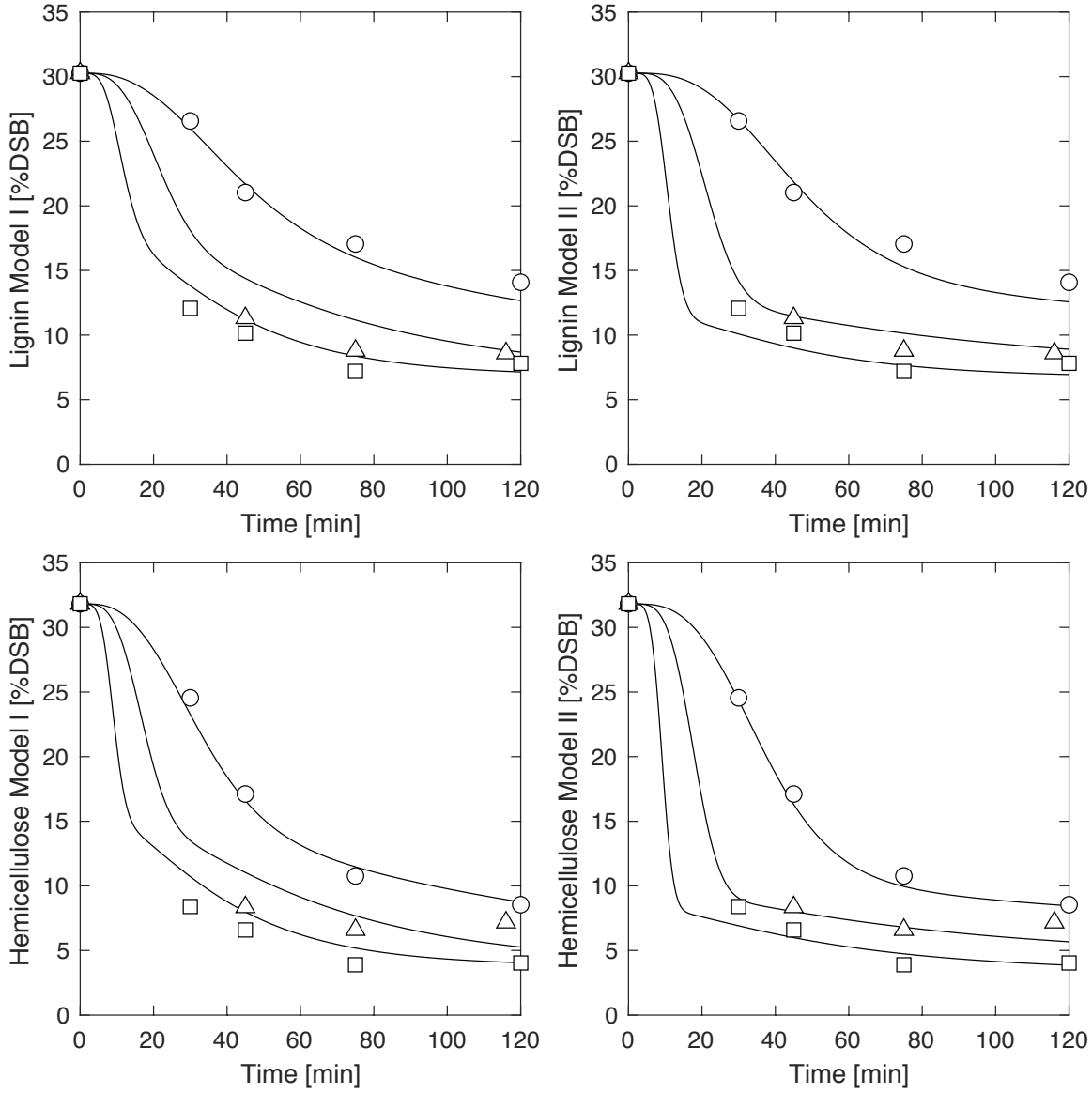
20
40
60
80
100
120
140
0
50
100
150

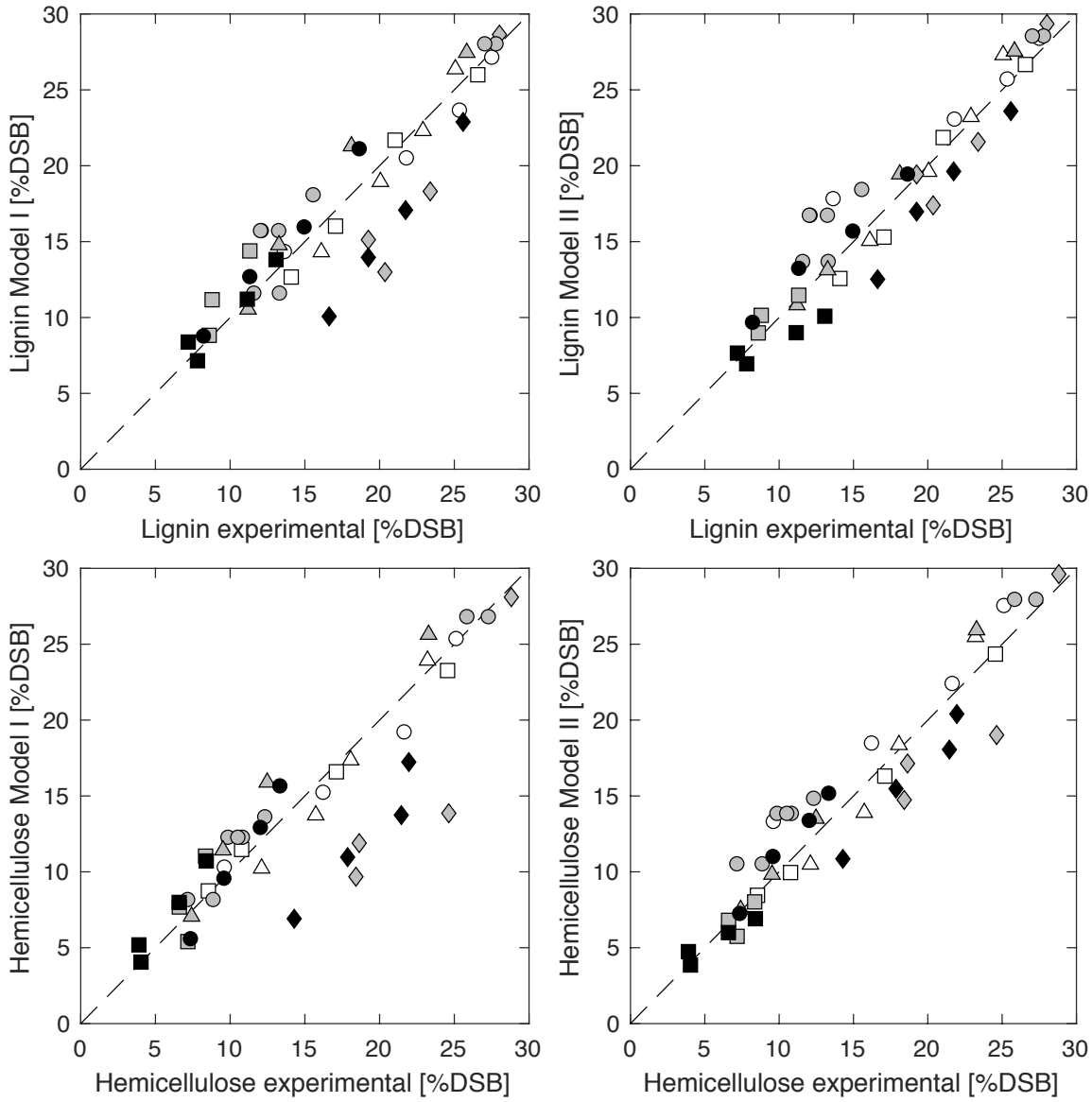

A
B
C
D
Raw
120
140
160
Mass fraction of almond sells [%DSB]
Temperature [°C]


0.4
0.3
0.2
0.1
0
Acetyl/Xylan [wt/wt]
120
130
140
150
160
Temperature [°C]
20
40
60
80
H2SO4 [mM]


A
B
C
D
Raw
25
35
45
75
Mass fraction of almond sells [%DSB]
H2SO4 [mM]


A
Cellulose [%DSB]
Time [min]
B
Lignin [%DSB]
Temperature [°C]
Time [min]
C
Hemicellulose [%DSB]
Time [min]
D
Acetyl/Saccharides [wt/wt]
Time [min]


Lignin Model I [%DSB]
Lignin Model II [%DSB]
Hemicellulose Model I [%DSB]
Hemicellulose Model II [%DSB]
Time [min]
0
5
10
15
20
25
30
35
0
20
40
60
80
100
120


Lignin Model I [%DSB]
Lignin experimental [%DSB]
Lignin Model II [%DSB]
Lignin experimental [%DSB]
Hemicellulose Model I [%DSB]
Hemicellulose experimental [%DSB]
Hemicellulose Model II [%DSB]
Hemicellulose experimental [%DSB]
0
5
10
15
20
25
30